15 (19)

ASD-TDR-62-416

(4) NA

(5) 418 500

(1)

AD No. 405436

FILE COPY

(6)

DELAYED ACTION, FOAM-IN-PLACE POLYURETHANE FOR USE IN AN AEROSPACE ENVIRONMENT

(7) NA

(8) NA

(9) Final rept Feb 61 - Jan 62,

TECHNICAL DOCUMENTARY REPORT No. ASD-TDR-62-416

(11) Mar 63,

(12) 100 p.

MARCH 1963

(13) NA

(14) NA

405 436

DIRECTORATE OF MATERIALS AND PROCESSES
AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

(20) U.

(21) NA

(16) (17)

Project No. 7381, Task No. 738101

DDC
RECEIVED
JUN 6 196
TISIA E

NO OTS

(15)

(Prepared under Contract No. AF 33(616)-7925 by the Hughes Aircraft Company, Culver City, California; Seymour Schwartz, author.)

63-05-5122 (10) by

NOTICES

ASTIA release to OTS not authorized.

Qualified requesters may obtain copies of this report from the Armed Services Technical Information Agency, (ASTIA), Arlington Hall Station, Arlington 12, Virginia.

Copies of this report should not be returned to the Aeronautical Systems Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

300 - April 1963 - 41

FOREWORD

This report was prepared by Hughes Aircraft Company as one phase of Contract No. AF 33(616)-7925, Project No. 1(8-7381) "Foamed-in-Place Plastic Materials in an Aerospace Environment." The work was administered under the direction of Materials Engineering Branch, Applications Laboratory of the Directorate of Materials and Processes, Aeronautical Systems Division. The work was initiated with Lt. David L. Wells as project engineer and was completed under the direction of Mr. Sidney Allinikov as project engineer.

This report covers work from February 1961 to January 1962. Eight monthly progress reports were written, including two quarterly progress reports. This report is issued under a slightly revised title as being more descriptive of the project.

Grateful acknowledgement is given Dr. Norman Bilow for his efforts in directing the early synthesis phase of the project, Mr. Boyce Kimmel for his work on water sources and structure fabrication and Mr. Irwin Zelman for his work on surfactants.

405436

ABSTRACT

This report details the materials and techniques were developed to meet the requirement of a delayed action, foam-in-place polyurethane for use in an aerospace environment.

The methods investigated for preparation of the special polyurethane included a number of chemical blocking reactions, molecular sieves and encapsulation techniques, all designed as restraining agents to inhibit the activity of the isocyanate component. The successful method finally developed utilized the principle of solid components to assure low reactivity and good storability. The optimum compound employed a sterically hindered solid diisocyanate, dianisidine diisocyanate, a solid diol, an ethylene oxide adduct of bisphenol A, a solid triol crosslinker, trimethylol propane, and a solid catalyst, dibutyl tin di-2-ethyl hexoate.

The resulting powder mixture was found to have storage stability of at least two months when stored at room temperature. The powder could be activated to produce foams of 2 to 5 pounds per cubic foot density on heating to 175 to 250°F in a vacuum environment. By addition of a water liberating blowing agent, boric acid, foams can also be made under ambient pressure conditions.

Structural components, made to demonstrate the utility of the powder, consisted of a seven-foot diameter balloon, which using predistributed powder on its surface, was inflated and rigidized at a simulated altitude of 150,000 feet, and a full sized man-supporting chair which was also made under the same conditions. In both cases infra-red heat was used as the triggering mechanism.

Publication Review

This technical documentary report has been reviewed and is approved.

W. P. Conrardy

W. P. Conrardy
Chief Materials Engineering Branch
Applications Laboratory
Directorate of Materials and Processes

CONTENTS

ILLUSTRATIONS

TABLES

I. INTRODUCTION

The advent of manned space flights, lunar and interplanatary explorations is daily coming closer to reality. In order to satisfactorily carry out these missions it will be necessary to erect structures in a space environment. These structures will not only provide laboratories and housing for space exploration, solar collectors for power, rigid balloons and antennas, etc., for communication; but structural elements will also be used for making beds, chairs, desks, etc., the transport of which would thereby be eliminated. Because of the current booster limitations, however, it is mandatory that the packaged weight and volume of these structures be restricted to a minimum.

The requirement for relatively large volume structures, coupled with small weight and initial volume, inevitably led to consideration of expandable and/or inflatable bodies. However, such thin walled structures would probably have marginal reliability, from the standpoint of gas leakage and micrometeorite resistance. Therefore a technique of rigidizing the structures, independent of gas pressures, was believed to be an approach which would result in a much superior product. One method by which this could be done would be to form the inflatable structure with gas and subsequently rigidize it permanently with a light-weight foamed-in-place material. If placed over the entire structure the foam material would serve then, not only as the structural element, but also as thermal insulation and micrometeorite protection, and possibly as an absorber of various radiations. The same foam-in-place material could also be used in construction of the required tables, chairs, etc.

A rigid, low density polyurethane foam plastic was considered to be the most promising material for this application. This program was therefore initiated to accomplish two objectives:

Manuscript released by the author March 1962 for publication as an ASD Technical Documentary Report.

1. Determine the feasibility of producing a polyurethane material which would foam in a space environment, and
2. Demonstrate the usage of such a material by rigidizing an inflated sphere and building a structural member in an aerospace environment.

Some additional requirements for the foam material were:

1. Foam density to be approximately 2 pounds per cubic foot.
2. The premixed foam system was to have a minimum shelf life of two months at room temperature.*
3. Initiation of the foaming reaction must not be time dependent.
4. The foaming reaction must take place in a vacuum using a completely vented enclosure, and minimum mechanical equipment.
5. Foaming must also take place at sea level pressure, with no basic change in formulation.

The structure capabilities were to be demonstrated by inflating, triggering and rigidizing a seven-foot diameter sphere in a manner compatible with unmanned operation in space.** The thick section capability was to be demonstrated by construction of a full sized chair in a space environment. Mechanical stirring, mixing or dispensing devices could be used in this phase, provided no special development or construction work was done. However, minimum mechanical equipment usage was desired.

---

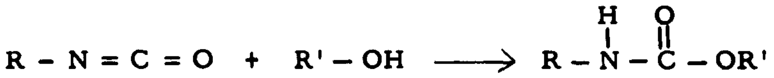
*Original requirement was 6 months.

**Original requirement was 10-foot diameter.

II. GENERAL CONSIDERATIONS

In the formulation of the foaming material there were several approaches which could be taken, since the disparity between the two structures called for essentially different materials. Inasmuch as the inflated structure was to be rigidized in a space environment by remote control, the only system involving a minimum of mechanical hardware was felt to be a predistributed system. Such a system, however, for the utmost in simplicity would have to employ a one-part formulation, and would probably require extensive development work. The chair, on the other hand, because of its relative compactness, lent itself ideally to a system utilizing mechanical metering, mixing and dispensing. The system for the chair then could be very similar to conventional liquid polyurethanes, with necessary modifications to material and/or equipment to permit foaming in vacuum. This system, however, probably could not be used for the inflated structure. After consideration of the factors involved in production of each type of system it was decided that if the one-part material were produced it would be a very simple approach and could be used for both applications, as well as being a potentially very useful material. It was therefore decided to concentrate solely on production of the one-part foamant. This then obviated development of two materials and equipment modifications which would be required.

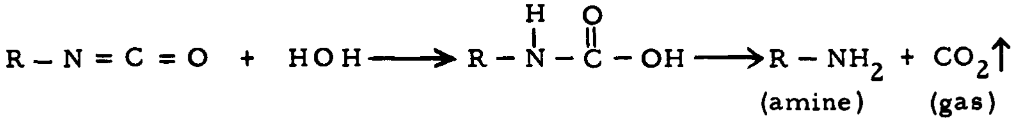
In the formation of a conventional polyurethane foam two or three liquid components are mixed together just prior to foaming. The urethane reaction usually is catalyzed to start in 5 seconds to a minute, and the exotherm produced during the reaction ranges from mild to high enough to cause charring of the final product. The basic reaction to form a urethane resin (solid), starting with an isocyanate and an alcohol is shown below:



$$R-N=C=O \;+\; R'-OH \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-OR'$$

(Isocyanate) (alcohol) (urethane resin)

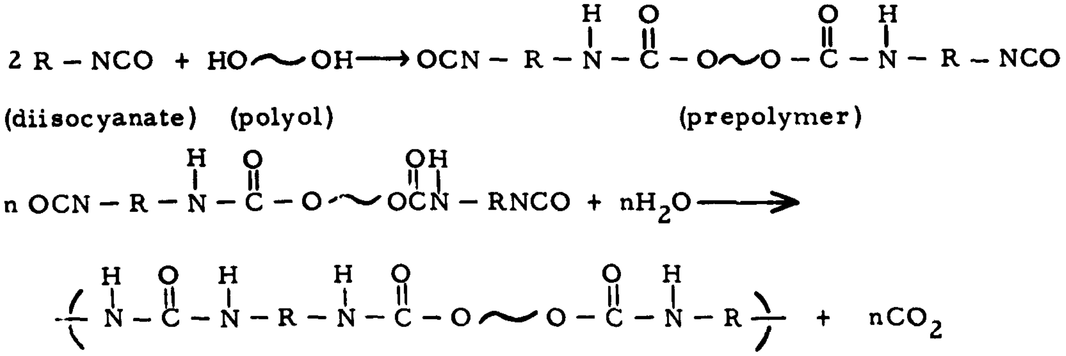
A secondary reaction of the isocyanate with water, to produce carbon dioxide gas is shown below:



$$R-N=C=O \;+\; HOH \longrightarrow R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \underset{\text{(amine)}}{R-NH_2} \;+\; \underset{\text{(gas)}}{CO_2\uparrow}$$

It may readily be seen that a combination of the two reactions would result in a foamed plastic, in which the urethane formed is the plastic resin and the CO_2 gas acts as the blowing agent. In actual practice the reactions are somewhat more complicated since both components must be at least difunctional in order to permit long chain polymerization. Furthermore, in order to obtain crosslinking, for strength at elevated temperatures, a portion of either the isocyanate or the hydroxyl bearing component (the usual case) should have three or more available functional sites. The usual commercial practice then is to use an 80:20 mixture of 2, 4 and 2, 6 tolylene diisocyanates as the isocyanate component and either polyesters or polyethers as the diol and triol sources. The final properties of the foam depend on the choice of the polyester or polyether, i.e., long chain linear polyols result in flexible foams while shorter chain length, highly branched polyols result in rigid, inelastic foams. The amount of crosslinking obtained in the final product may easily be varied by blending linear and branched chain polyols.

A representation of the actual reactions in a typical polyurethane foam is as shown below:



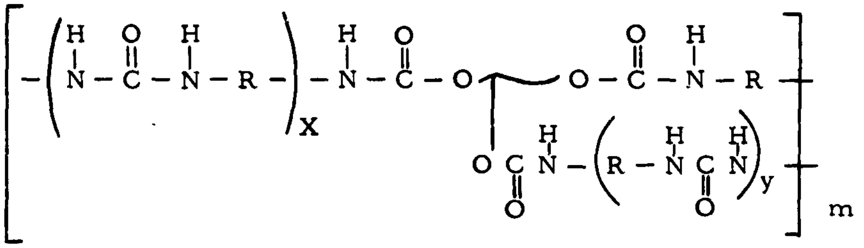
$$\underset{\text{(diisocyanate)}}{2\,R-NCO} \;+\; \underset{\text{(polyol)}}{HO\sim OH} \longrightarrow \underset{\text{(prepolymer)}}{OCN-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\sim O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-NCO}$$

$$n\,OCN-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\sim O\overset{O}{\overset{\|}{C}}\overset{H}{\overset{|}{N}}-RNCO \;+\; nH_2O \longrightarrow$$

$$\left(\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O\sim O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R\right) \;+\; nCO_2$$

urea linked polymer

A crosslinked polymer, obtained by the use of a branched resin, would have the following idealized structure:



In addition to the major reactants shown above a catalyst is also included to drive the reaction between the isocyanate, resin and water at such a rate that the foam rises and cures sufficiently fast to prevent collapse of the foam. The gas evolution and the polymer growth must be matched so that the gas is trapped efficiently and the polymer has the right strength at the end of the gas evolution to maintain its volume without collapse or gross shrinkage. Catalysts commonly employed are tertiary amines and organo-tin compounds, either separately or in combination. Lastly a surfactant, or surface active agent, is included to act as a surface tension depressant and cell size regulator. Materials such as methyl silicone oils and fatty alcohol derivatives are commonly used as surfactants.

In the above description of the basic chemistry of "typical" polyurethane foam formulations[*] it should be borne in mind that all the ingredients commonly used to make such foams are free flowing liquids at room temperature. Furthermore on mixing the components usually react very quickly (within a few seconds) and the resulting exotherm raises the vapor pressure of the separate ingredients, and the mixture, to well above that which could be tolerated in a vacuum atmosphere. The task of making the desired one component, vacuum foamable material then resolved to two main problems.

---

[*] Other, side reactions, also occur but are not being dealt with here.

1. Materials must be obtained which, when intimately mixed, would not react with each other until triggered.
2. The materials must have sufficiently low vapor pressures at the reaction temperatures to allow polymerization, and foam formation, under vacuum conditions.

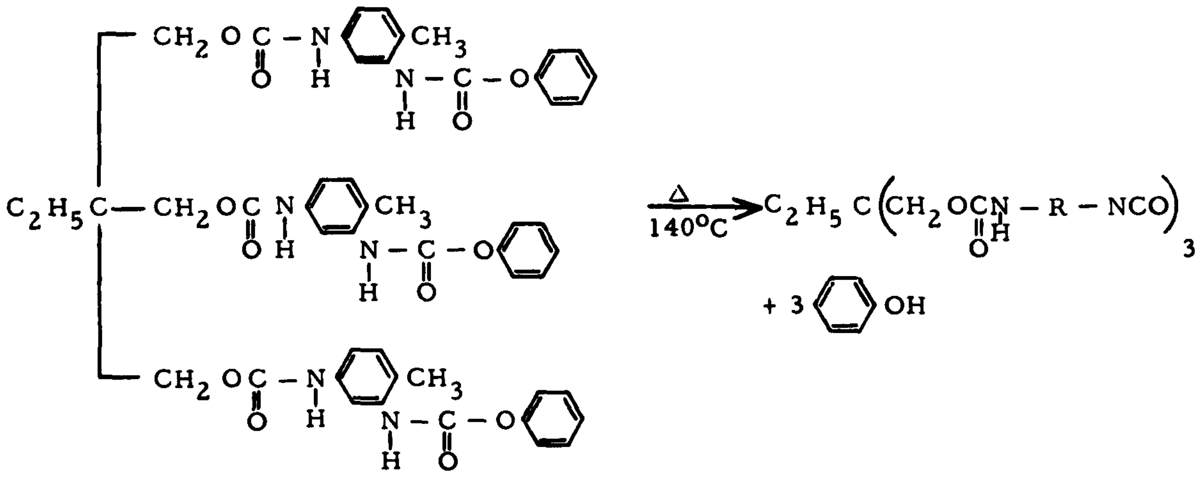
In attempting to obtain foam ingredients which could be mixed together without reaction it was early decided that some means would have to be used to "deactivate" the reactive isocyanate and that heat would be used as the triggering mechanism to start the reaction. A number of different systems for "deactivating" the reactive components therefore were selected for investigation. These included the following.

1. Chemically blocked isocyanates (heat cleavable).
2. Procurement and/or preparation of solid isocyanates and polyols. (To be liquified by heat.)
3. Encapsulation of the isocyanate component. (The capsules to be broken by heat allowing the isocyanate to react with the polyols.)
4. Physical entrapment of various components. (Included the use of molecular sieves and water of hydration held by various salts.)

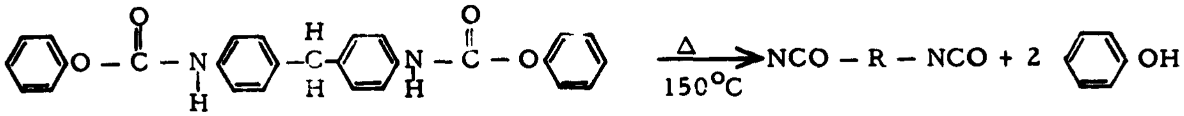
III. EXPERIMENTAL

A. INVESTIGATION OF CHEMICALLY BLOCKED ISOCYANATES

In the investigation of blocked isocyanates materials were obtained from two commercial sources and were also synthesized in the laboratory. The two commercial blocked isocyanates were Mondur S, a phenol blocked trimethylolpropane adduct of tolylene diisocyanate, obtained from the Mobay Chemical Co., and Hylene MP, the di-phenol adduct of methylene bis (4-phenylisocyanate) obtained from the DuPont Co. The structural formulas and the reversible reactions yielding the reactive isocyanates are shown below.



Mondur S cleavage reaction



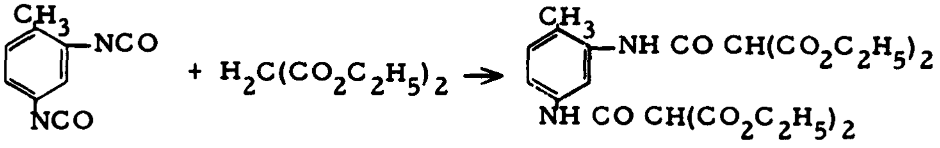
Hylene MP cleavage reaction

Blocked isocyanates prepared by synthesis included reactions of tolylene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), with diethyl malonate, acetyl acetone, p-nitro phenol, sodium bisulfite, phthalimide and picric acid. In each case synthesis was undertaken with a view toward obtaining a material which might cleave faster and at a lower temperature than was obtainable with the commercially available materials.

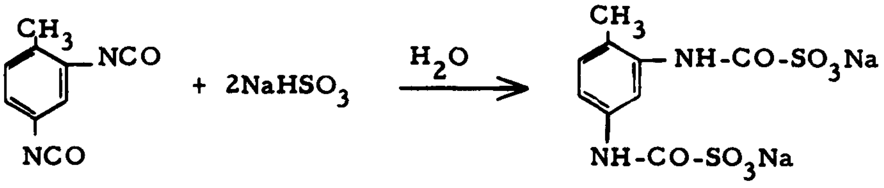
Acetylacetone

$$2H_2C(COCH_3)_2 + CH_2(C_6H_4NCO)_2 \rightarrow CH_2\left[C_6H_4\text{-NH-CO-CH}(COCH_3)_2\right]$$

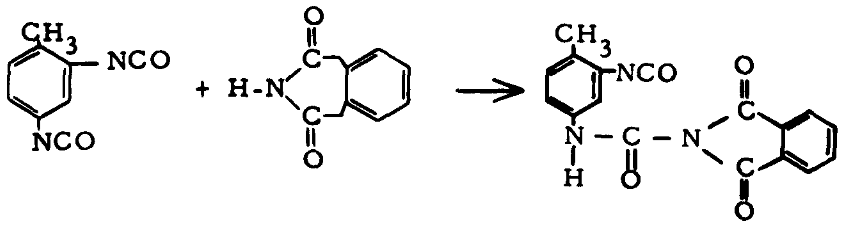
Diethylmalonate



Sodium Bisulfite

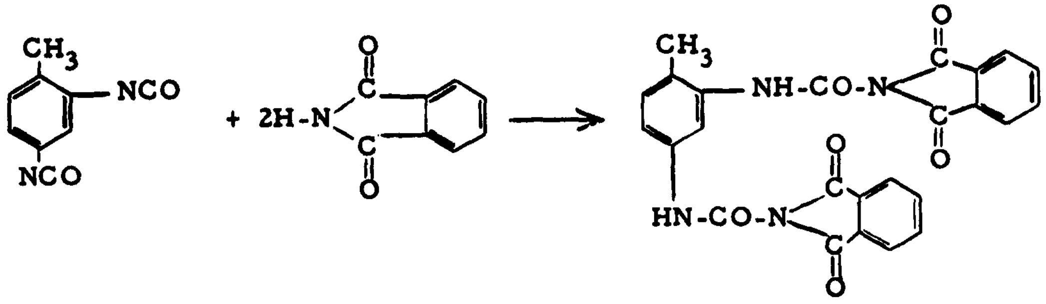


Phthalimide



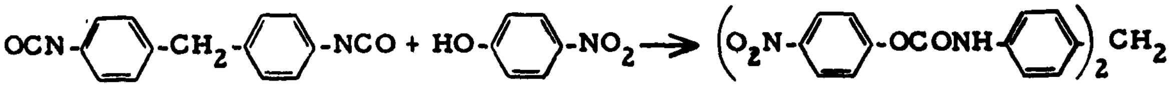
1:1 adduct

Phthalimide

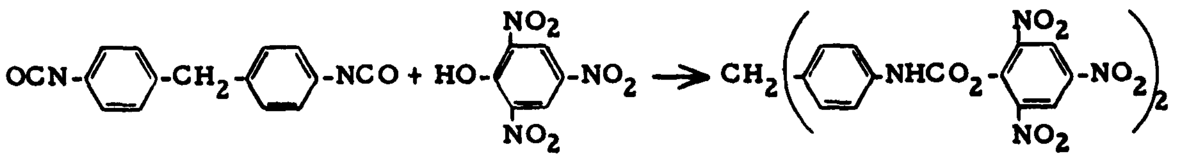


2:1 adduct

p-Nitrophenol



Picric Acid

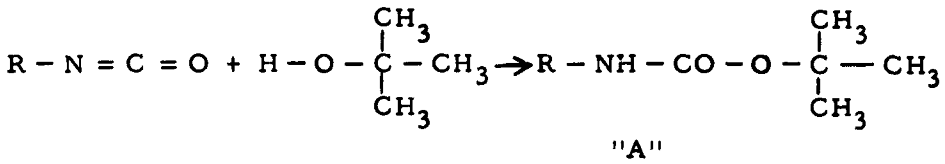


One of the most interesting (but disappointing) observations made in this investigation was the fact that sodium bisulfite blocked isocyanates cleaved rather sharply at about 65°C in an aqueous solution with the concomitant evolution of carbon dioxide, whereas temperatures above 180°C were required for cleavage to occur in the dry state or in formulations with other polyurethane ingredients.

Of the various blocking agents investigated, phthalimide appeared to be about the best, not because of a lower cleavage temperature (about 180°C), but primarily because of its slightly higher rate of cleavage at this temperature. As compared to phenol, the presence of a nitro group on the aromatic ring lowers the cleavage temperature of the adduct. This is indicated by the observation that phenol blocked isocyanates do not cleave at a satisfactory rate below 190°C, whereas the p-nitrophenol adduct cleaves closer to 170°C. Having made this observation it seemed reasonable to utilize picric acid (trinitrophenol) to obtain even lower cleavage temperatures. In carrying out the picric acid synthesis, however, it appeared that the reaction takes an abnormal course, possibly involving an oxidation of the isocyanate group.

After preparation the various blocked isocyanate compounds described above,as well as the commercial phenol blocked diisocyanates, were formulated with stoichiometric amounts of commercial liquid polyols (such as Archer-Daniels Arapol 7845) and catalysts. Formulated samples were then heated until the polymerizations were essentially complete and the products had become completely rigid. In all instances, no significant rigidization occurred until the samples had been heated to a minimum of 170°C for a period of at least ten to fifteen minutes. When foamable formulations were prepared, the foams always collapsed prior to rigidization due to the rapid loss of blowing gases at the high temperatures as well as the low polymerization rates. In vacuum foaming studies copious quantities of gases were formed by the relatively low boiling blocking agents. Acetylacetone, for example, boils near room temperature at pressures as high as 8 mm Hg, and diethylmalonate and phenol boil at room temperature at pressures of about 2 mm Hg. It is apparent, therefore, that although trace quantities of these blocking agents could act as their own blowing agents, the quantities of the materials required to block all of the isocyanate groups in a polyurethane formulation would yield copious quantities of gases when the foaming process is carried out in vacuum. Hydrogen chloride and hydrogen cyanide were not investigated as blocking agents even though they tend to unblock at lower temperatures. Besides being low boiling gases, the extreme corrosiveness of hydrogen chloride and the extreme toxicity of hydrogen cyanide make these materials unsuitable for use in a versatile delayed action polyurethane formulation.

Tertiary alcohols were also investigated as isocyanate "blocking" agents. Actually, the isocyanate adducts are not properly classed as blocked since their thermal cleavage does not regenerate free isocyanate groups. A generalized illustration of the mode of addition and mode of cleavage is as follows:



$$R - N = C = O + H - O - \underset{CH_3}{\overset{CH_3}{C}} - CH_3 \rightarrow \underset{\text{"A"}}{R - NH - CO - O - \underset{CH_3}{\overset{CH_3}{C}} - CH_3}$$

$$\text{"A"} \xrightarrow[135^\circ C]{heat} RNH_2 + CO_2\uparrow + CH_2 = C(CH_3)_2$$

In the above reaction it will be noted that the net effect of the cleavage is essentially the same as if normal unblocking had occurred followed by reaction with water. This type of reaction would be more applicable to the preparation of delayed action polyurethane foam mixtures for use at ambient pressures than for use at very low pressures, since supplementary inhibiting methods would be essential in vacuum foaming applications. This is evident due to the fact that when t-alcohol inhibition is used alone the volume of gas liberated on decomposition far exceeds the amount of gas required for foaming in vacuum.

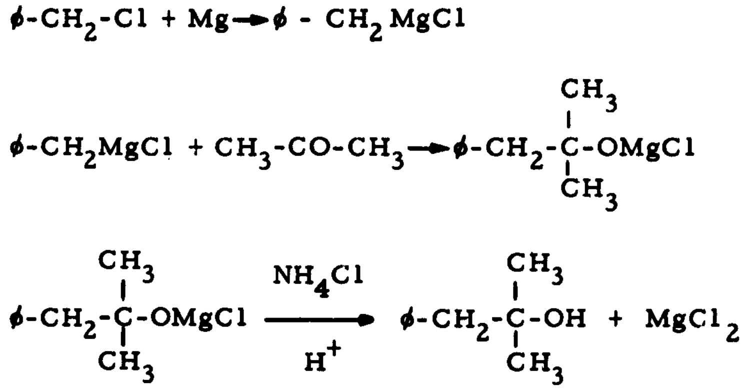
It is furthermore important to note that not more than 50 percent of the available isocyanate groups should be blocked with the tertiary alcohol if complete crosslinking is to occur, since the extra isocyanate groups are required to react with any amino groups which are liberated during the cleavage reaction. This may be illustrated as follows:

$$R - NH_2 + R'NCO \rightarrow R - NH - CO - NH - R'$$

To be useful in vacuum foaming applications, no more than 5 percent of the available isocyanate groups should be blocked with tertiary alcohols, otherwise excessive gas evolution would occur. It thus becomes obvious that methods must first be developed for the deactivation of the remaining 95 percent (or more) of the available isocyanate groups.

In a typical investigation a commercial isocyanate prepolymer was reacted with 50 molar equivalent percent of tertiary amyl alcohol and a molar equivalent amount of a commercial polyol. The reaction mixture polymerized to an extremely viscous product which, when heated to 130-140°C, gave a rigid foamed structure. In vacuum the product foamed excessively.

In the anticipation that benzyldimethylcarbinol would cleave at a lower temperature, this alcohol was synthesized as illustrated below:



$$\phi\text{-}CH_2\text{-}Cl + Mg \rightarrow \phi - CH_2MgCl$$

$$\phi\text{-}CH_2MgCl + CH_3\text{-}CO\text{-}CH_3 \rightarrow \phi\text{-}CH_2\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}\text{-}OMgCl$$

$$\phi\text{-}CH_2\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}\text{-}OMgCl \xrightarrow[H^+]{NH_4Cl} \phi\text{-}CH_2\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}\text{-}OH + MgCl_2$$

Reaction of the benzyldimethylcarbinol with a commercial polyisocyanate and polyol yielded an inhibited system which showed no significant gas evolution until it was heated above 130°C with decomposition being rapid at 160-170°C.

It is worthy of note that the basic catalysts used in the addition of alcohols to isocyanates also appeared to catalyze some premature dehydration. This may be minimized by carrying out the "blocking" reaction at low temperatures, preferably below 5°C. Although additional work with tertiary alcohols was warranted, it became necessary to study other inhibition methods, since t-alcohol "blocking" could be used on only a small portion of the isocyanate groups as previously explained.

One other test was run on blocked isocyanates which was regarded as highly significant. A stoichiometric mixture of Mondur S and Arapol 7845 was set aside for storage test at room temperature. After several days distinct hardening of the mixture was noted, indicating either incomplete blocking or cleavage at a much lower temperature than was anticipated.

As a result of the work done with all the various blocking systems, it was concluded that none of these systems offered much promise because of slow cleavage at too high temperatures and excessive gas evolution.

B. SOLID SYSTEMS

The slow reaction rates and relatively high cleavage temperatures found with the blocked isocyanates indicated that these systems would never be entirely satisfactory even if good storage properties could be obtained when mixed. Attention was therefore directed to development of completely solid systems. It was reasoned that mixtures of such systems should have the stability required for good storage life. Polymerization would then be triggered by melting the mixture. If isocyanates, polyols, water sources, catalysts and cell size regulators with low enough vapor pressures at the melting temperatures could be obtained then it was felt vacuum foaming could be accomplished. The ideal main ingredients (isocyanates and polyols) then required for such a space foam formulation would be crystalline solid reactants, all having a melting point between 50 to 80°C (arbitrarily selected as being high enough to be safe under normal storage conditions, and yet not too high as to cause degradation to possible substrates, or be impossible to attain by solar heat without use of concentrators),virtually no vapor pressure at the melting temperature, and a molecular weight below 500, in order to insure rigidity in the final product.

In addition, of course, it was necessary that the solids show sufficient reactivity to polymerize soon after onset of the melting reaction. However, melting and polymerization must take place at a rate which would not preclude foam formation or allow collapse after the maximum foaming.

In order to establish the feasibility of the solids approach, a simple formulation was developed which, while not meeting all the above requirements, did develop a foam when heated at ambient pressures. When heated in a vacuum it frothed and foamed excessively due to the high vapor pressure of the components. It nevertheless definitely indicated the possibility of the solids approach. Using this formulation as a "standard" it was then planned to investigate the effects of substituting various other ingredients to improve its properties. The "standard" formulation had the composition shown as follows.

Material	Function	Equivalent Weight	Equivalents Used	Grams
Diphenyl 4,4' diisocyanate (Nacconate 300-MDI)	Isocyanate	125	0.05	6.2
Bisphenol A	Diol	114	0.041	4.7
Pyrogallol	Crosslinker	42	0.01	0.4
Boric Acid	Water source		5% by weight	0.5
Silicone Oil Union Carbide L-520	Surfactant		1% by weight	3 drops
Catalyst	8 hydroxy-quinoline		5% by	0.55

In the above formulation the silicone oil was first melted together with the diol, then after resolidification all of the ingredients were ground together to a fine powder. Upon melting at 130-150°C, the mixture foamed to a rigid, friable structure. In these, and most other ambient pressure tests, the materials were heated in small aluminum cups, which were held in specially constructed aluminum plates, as shown in Figure 1. With this setup, samples usually 4 grams, could be placed in the cup and heated at known temperatures in a uniform manner repeatedly, using either conducted heat, infra-red heat, or a combination of both. Oven heating was also used, but this setup was preferred because of ease of observation during the reaction.

Samples to be foamed in a vacuum were tested in the apparatus shown in Figure 2. With this equipment it was possible to heat the samples at any desired rate by infra-red or by a combination of infra-red and conducted heat (using a hot plate in the bell jar), to temperatures as high as 500°F, at any pressure from ambient down to approximately 0.7 mm Hg. However, since the materials were to work at 165,000 feet (0.7 mm Hg) all the vacuum tests were conducted at that pressure. Temperature recording was available by the use of thermocouples which were embedded in samples. Density determinations were made by simply measuring the height and weight of samples foamed in tin cans, and using previously calculated factors. Other determinations were made by measurements of volume and weight of samples such as shown in Figure 6. More accurate determinations were made by placing samples of foam in large graduates and then filling the graduate with

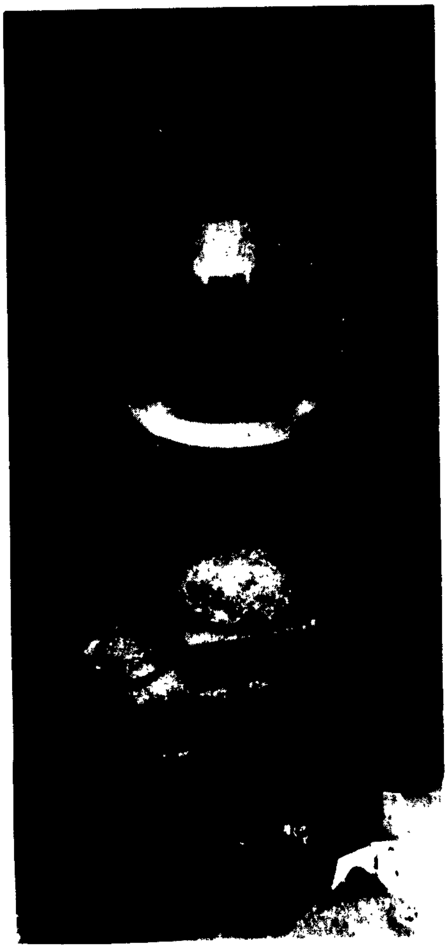
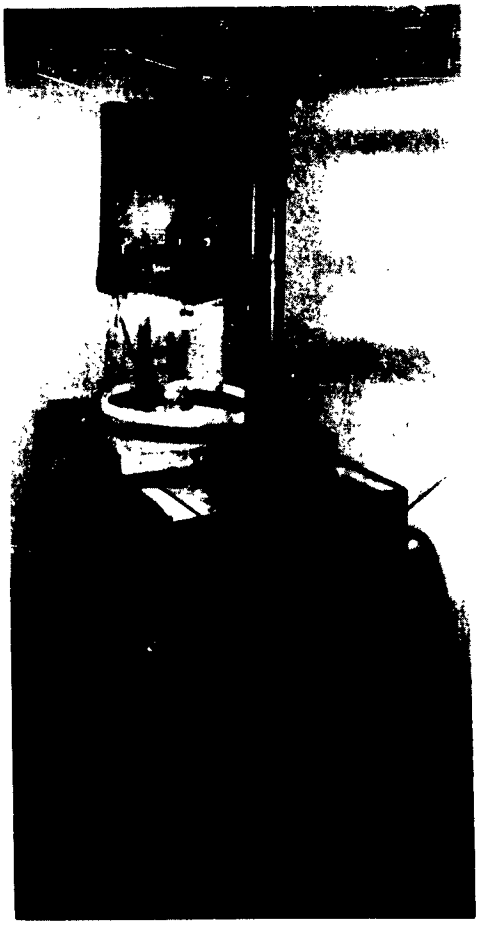


Figure 1. Ambient pressure foam powder heating apparatus.

Figure 2. Vacuum foaming equipment.



fine shot. From the weight of shot used to fill the graduate to a known volume quite accurate density measurements could be made.

Having established a basic type of formula, it became necessary to reduce its friability, improve its vacuum foaming ability and, if possible, reduce the reaction temperature. Several hundred formulations were then prepared in which other reagents were substituted for those in the "standard." The quantities substituted were such that stoichiometric molar ratios were generally maintained, and if two different diols or two different diisocyanates were used simultaneously the molar sums were kept constant. Every formulation was not investigated in vacuum, but many were. If, upon atmospheric pressure foaming, a nonrigid or excessively brittle foam was obtained, for example, its evaluation in vacuum was not performed. Like the approach which was taken in the blocked isocyanate investigation, both commercially available materials and specially synthesized materials were tested.

In the case of the diisocyanate materials two approaches were also taken. First all known, commonly available, low melting solid isocyanates and solid blocked isocyanates were tested, using the "standard" formulation. These materials are listed in Table I.

Source	Designation	Type	Equivalent Weight	M. P. °C	Comments
Allied Chemical Co.	Nacconate 300 (MDI)	diphenyl 4,4' diisocyanate	125	37	Vaporized too much in vacuum.
Allied Chemical Co.	Nacconate 200 (TODI)	3,3'bitolylene 4,4'diisocyanate	132	69	Vaporized in vacuum and reacts to slowly.
Carwin Co.	DADI	dianisidine diisocyanate	149	120	Reacts too slowly.
DuPont Co.	Hylene MP	phenol adduct of methylene bis(4 phenylisocyanate)	220	150	Cleavage temperature too high.
Mobay Chemical Co.	Mondur S	phenol adduct of tolylene diisocyanate	235	150	Cleavage temperature too high.

Table I. Commerically available solid isocyanates.

Concurrent with the tests being run with the various solid isocyanates, a number of solid diols and polyfunctional crosslinking agents were also substituted in the "standard" formula. These materials were all selected for possible use on the basis of: (a) they were solids, (b) they had the correct functionality, (c) the molecular weight and structure was such that a good resin might result, (d) the melting point was in the right range and (e) the vapor pressure might be satisfactory. The materials tested are shown in Table II.

Diols	Action When Heated In Vacuum	Action When Used In The "Standard" Formula
2,5-dimethyl-2,5-hexanediol	Vaporizes	Will not rigidize
2,3-dimethyl-2,5-hexynediol	Vaporizes	Will not rigidize
3,6-dimethyl-4-octyne-3,6-diol	Vaporizes	Will not rigidize
ethynyl dicyclohexanol	Vaporizes	Will not rigidize
1,6 hexanediol	Vaporizes	Granular
neopentyl glycol	Vaporizes	Friable
tetrachlorobisphenol A	Vaporizes	Friable
p,p'-dihydroxy-2,2-diphenyl propane	Vaporizes	Friable
p,p'-dihydroxy-2,2-dicyclohexyl-propane	Vaporizes	Friable
polyethylene glycol 6000, 9000 M. W.	None	Granular soft polymers
Crosslinkers		
Trishydroxymethylamino-propane	Vaporizes	Polymerizes too fast, poor miscibility in melt
2-amino-2-methly-1,3-propanediol	Vaporizes	Polymerizes too fast, poor miscibility in melt
pyrogallol	Vaporizes	Friable
trishydroxymethylpropane	Vaporizes	Friable
sorbitol	None	Non miscible with other reactants

Table II. Solid polyols.

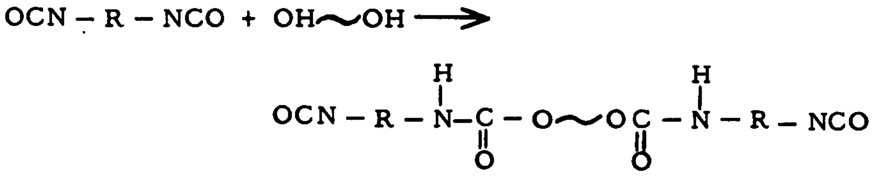
A number of commercially formulated solid polyols were also procured and tested for reactivity with the isocyanates. With one exception these resins were all unsatisfactory either because of high viscosity at the melting point, or too high a molecular weight (resulting in a rubbery structure) or the foam produced was extremely friable, etc. The one satisfactory resin found was Atlas G-1672 (later procured from Dow Chemical as X-2635). The list of solid polyols tested is shown below in Table III.

Source	Designation	Type	Eq. Wt.	M. P. °C	Comments
Atlas Powder Co.	G-1672	Polyester	166	100	Fair foam
Atlas Powder Co.	363E	Polyester	1600	95-105	Too rubbery
Atlas Powder Co.	382E	Polyester	1600	80-85	Too rubbery
Atlas Powder Co.	Isosorbide	Polyether	73	62	Friable
DuPont Co.	Terracol 30	Polyglycol	1470	38	Too rubbery
Mobay Chem. Co.	R-14	Polyester	1000	44	Rubbery and tough
Mobay Chem. Co.	R-38	Polyester	415	90	Fair foam slightly rubbery

Table III. Commerically formulated solid polyols.

The direct combination of the solid diisocyanates with the available solid polyols was apparently resulting in polymers either too soft, too friable, too volatile, etc. Therefore, after testing approximately half the above ingredients it was decided to use isocyanates and polyols which were designed for use in urethane foam or resin formulations, so that the correct functionality, structure and molecular weight would be available at the start. However, since these were largely liquid materials it was decided to solidify them by use of a "prepolymer" technique.

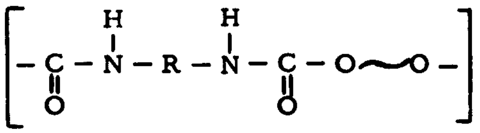
The second approach then to obtaining solid ingredients was to procure commercially, and to prepare by synthesis, polyurethane "prepolymers." In this sense the term "prepolymer" refers to urethane-linked chains resulting from a nonstoichiometrical reaction of the diisocyanate and a hydroxyl terminated polyester or polyether. The "prepolymer" is terminated in either –NCO or –OH groups, depending on which reactant is present in excess. The general reactions for an excess of isocyanate are shown below.



$$\mathrm{OCN-R-NCO + OH\sim OH} \longrightarrow$$

$$\mathrm{OCN-R-}\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{O\sim O}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}\mathrm{-R-NCO}$$

the repeating unit is



$$\left[-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}\mathrm{-R-}\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}-\mathrm{O\sim O}-\right]$$

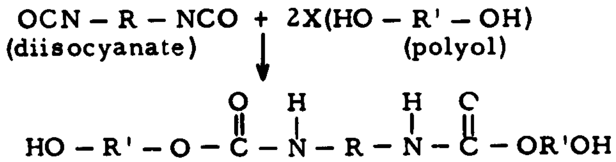
Isocyanate termination (as shown) was utilized in two solid prepolymers obtained commercially from the Mobay Chemical Co. These materials are listed in Table IV. The material designated as CB-75 was originally obtained as an ethyl acetate solution from Mobay and was isolated by vacuum evaporation of the solvent.

Source	Designation	Type	Eq. Wt.	M.P. °C	Comments
Mobay Chem. Co.	F-66	isocyanate-polyester prepolymer	640	45	Reacted too slowly, did not foam.
Mobay Chem. Co.	CB-75	trimethylol propane-tolylene diisocyanate prepolymer	250	100	Good reactivity and foaming. See below for further comments

Table IV. Commerically available isocyanate terminated pre-polymers.

In addition to the –NCO terminated prepolymers obtained from commercial sources a number of solid hydroxyl terminated prepolymers were also prepared. The most promising materials found at first were high viscosity liquid polyesters and polyethers which were reacted with an isocyanate, diphenylmethane 4,4'diisocyanate (Nacconate 300, MDI). It was found that, by careful control of the exotherm, a solid polyol could be obtained by the addition of a considerably less than the stoichiometric amount of MDI to the heated polyol. After the exotherm had subsided and on cooling the resulting material was hard and could be powdered. In this reaction, shown below, a hydroxyl terminated isocyanate-prepolymer was obtained, which could be later reacted with additional isocyanate to complete the urethane polymer. In practice it was found that the limits between the amount of isocyanate required to cause solidification (when cool) and that which gave a thermosetting resin were quite narrow.

Typical Reaction



$$\underset{\text{(diisocyanate)}}{OCN-R-NCO} + \underset{\text{(polyol)}}{2X(HO-R'-OH)}$$

$$\downarrow$$

$$HO-R'-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-R-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-OR'OH$$

In the above, X could vary from 1-1/2 to 3, depending on the final viscosity desired, i.e., if 2X = 6 the material has the lowest viscosity when molten, but unfortunately exhibited extremely bad caking tendencies when standing. The caking tendency could be alleviated by addition of 1-1/2 percent Cabosil. The best solid polyol prepared in this manner utilized Allied Chemical Company Nacconate 300 (MDI) and Mobay Chemical Company Multron R-2 polyester in the ratio of 1 equivalent of Nacconate 300 to 5 equivalents of the Multron R-2. This material, on one to two weeks storage at room temperature was also found to cake, so possibly the ratio should have been 4.5 to 1. A list of the polyols investigated, using this technique, is shown in Table V.

The initial solid hydroxyl terminated prepolymers were not entirely satisfactory, since they did not store well. The poor storage (caking) was apparently due to continued polymerization, as evidenced from the fact that the melting point and viscosity increased and reactivity decreased, so a foam would not form, or it would have a very high density. Therefore a series of isocyanate prepolymers were prepared, along with a series of

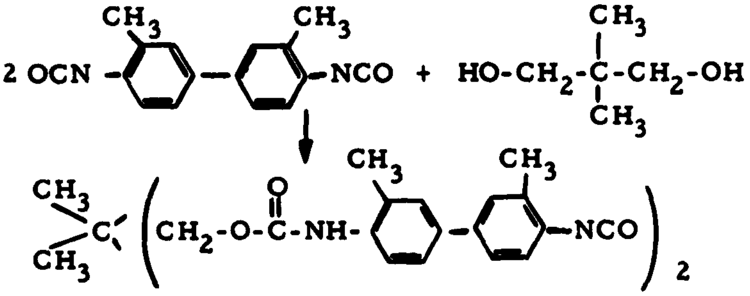
Source	Designation	Type	Eq. Wt.	Comments
Mobay Chem. Co.	Multron R-2	Polyester	142	Made a good foam
Mobay Chem. Co.	Multron R-4	Polyester	190	Fair
Wyandotte Chem. Co.	Pluracol SP-560	Polyether	85	Reacts too fast
Wyandotte Cham. Co.	Quadrol	Polyether	75	Reacts too fast
Union Carbide	LS-490	Polyether	115	Fair
Atlas Powder Co.	G-2406	Polyether	86.5	Reacts too fast

Table V. Commerically available polyols used in preparation of hydroxyl terminated pre-polymers.

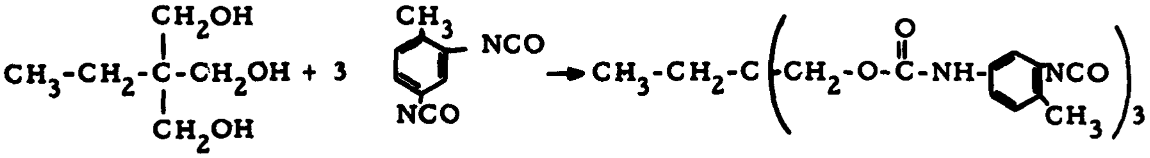
polyesters. In each case the molecular weights and functionality were chosen so that, if the resulting materials were solids and melted in the right range, they would also yield tough, nonfriable foams. These synthesis are illustrated below, showing the reaction courses taken.

DIISOCYANATE PREPARATIONS

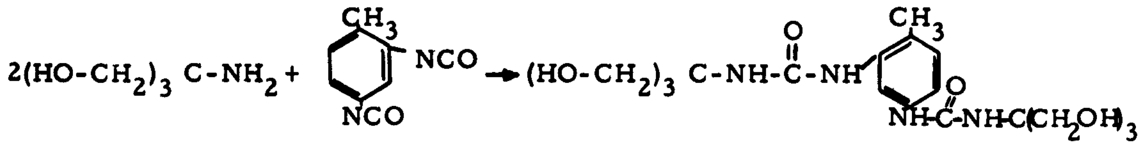
Reaction of Neopentylglycol with 3,3'-bitolylene-4,4' diisocyanate (B2297-43)



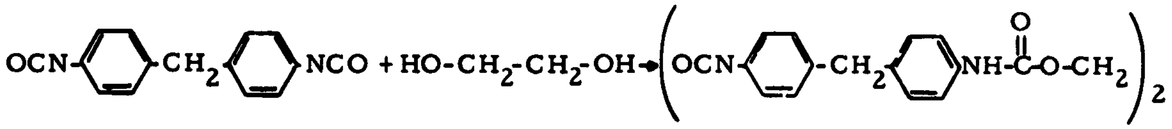
Reaction of Trimethylolpropane with 2, 4-toluenediisocyanate (B2351-18B)



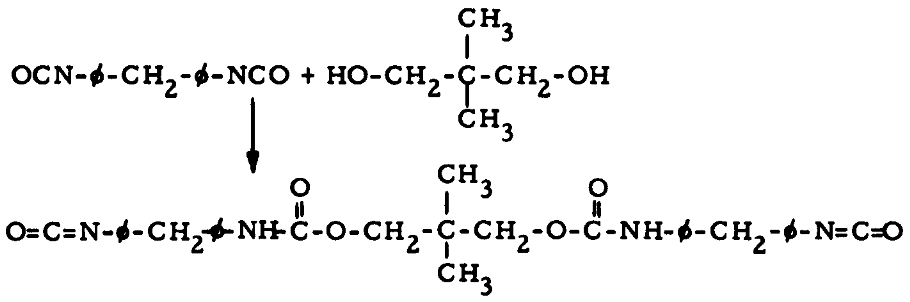
Reaction of Tris(hydroxymethyl)aminomethane with 2, 4-Toluenediisocyanate (B2351-18C)



Reaction of Diphenylmethane-p, p'-diisocyanate with Ethylene Glycol (B2351-19B)



Reaction of Neopentylglycol with Diphenylmethane-p, p'-diisocyanate (B4015-2)

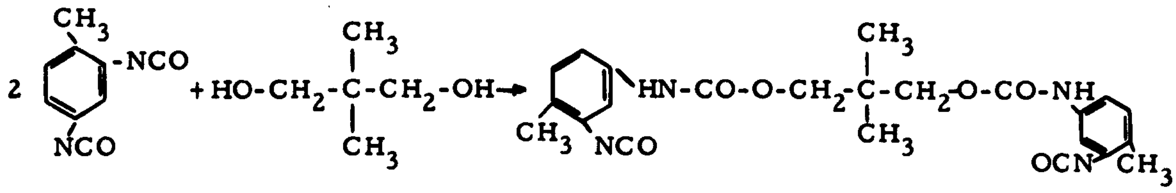


$$\mathrm{OCN{-}\phi{-}CH_2{-}\phi{-}NCO + HO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}OH}$$

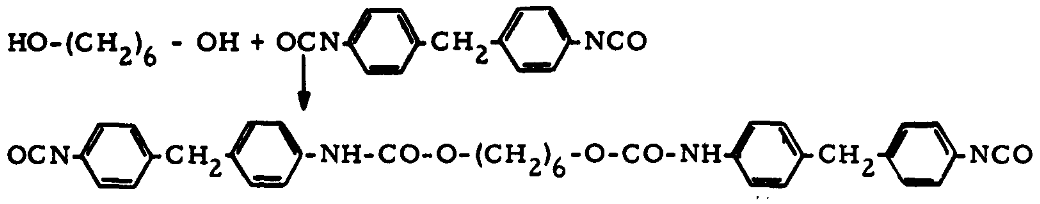
$$\downarrow$$

$$\mathrm{O{=}C{=}N{-}\phi{-}CH_2{-}\phi{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}\phi{-}CH_2{-}\phi{-}N{=}C{=}O}$$

Reaction of Neopentylglycol with 2, 4-Toluenediisocyanate (B2297-48)

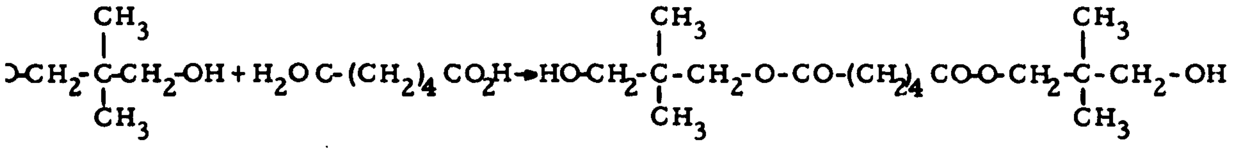


Reaction of Hexamethyleneglycol with Diphenylmethane-p, p'-diisocyanat (B3615-34, 46A, 46B)



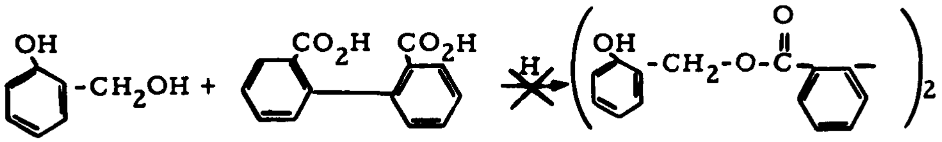
POLYESTER PREPARATIONS

Neopentylglycoladipate (B3615-15)

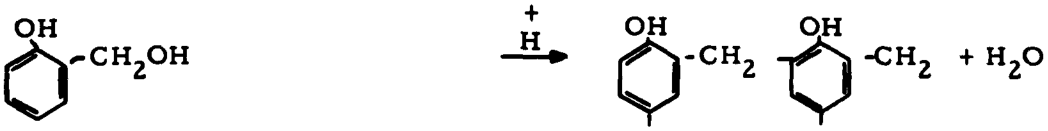


$$\mathrm{{}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH + H_2O\,C-(CH_2)_4\,CO_2H \rightarrow HO-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-O-CO-(CH_2)_4\,CO-O-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-OH}$$

Ester of o-hydroxybenzylalcohol and Diphenic Acid (B2297-47)

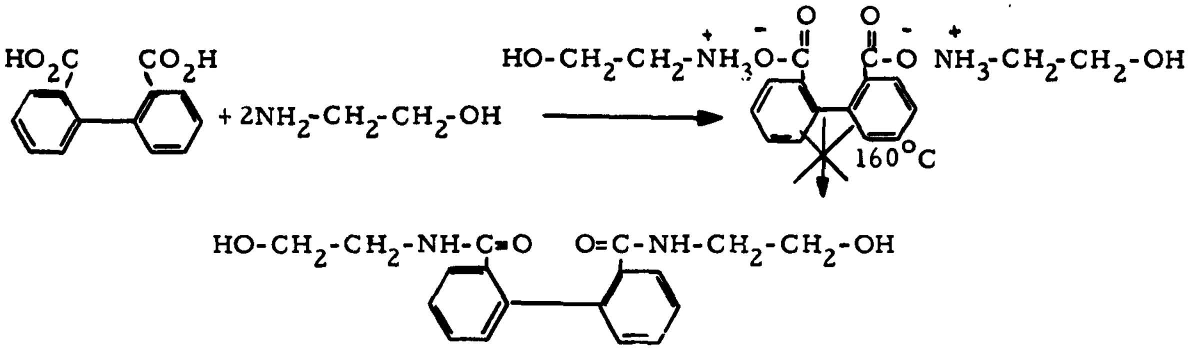


desired reaction

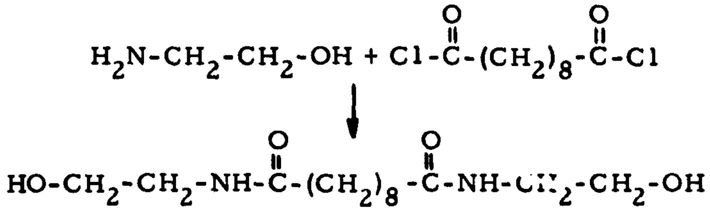


actual reaction

Amide of Ethanolamine and Diphenic Acid(B4015-5 and B2297-49)

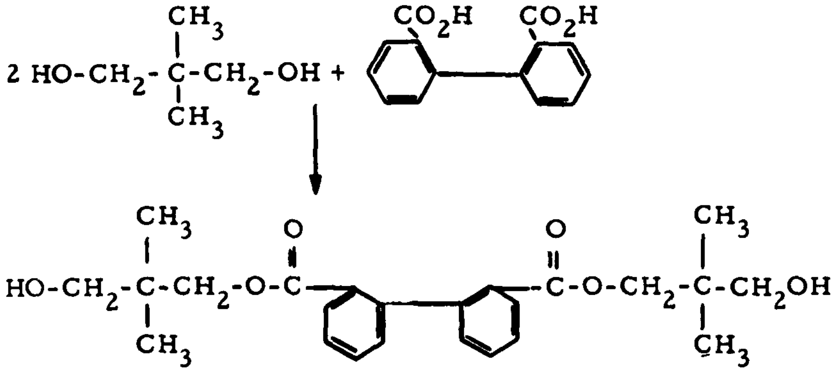


Diamide of Ethanolamine and Sebacoylchloride (B2351-19A and B2297-51)

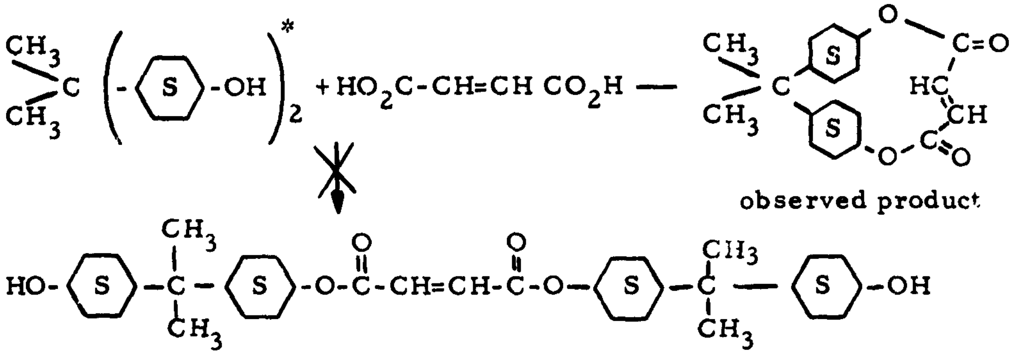


$$\begin{gathered}H_2N\text{-}CH_2\text{-}CH_2\text{-}OH + Cl\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_8\text{-}\overset{\overset{O}{\|}}{C}\text{-}Cl\\ \downarrow \\ HO\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_8\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}OH\end{gathered}$$

Ester of Neopentylglycol and Diphenic Acid (B3615-14)

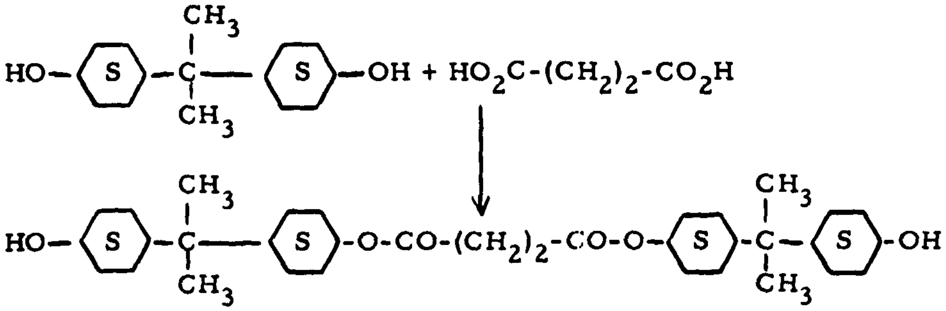


Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Fumaric Acid (B3615-40)

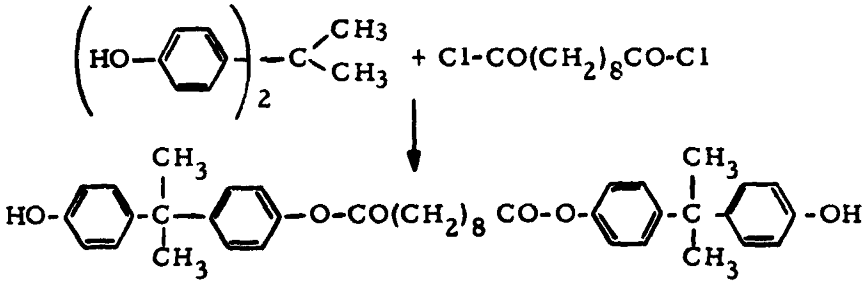


expected product

Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Succinic Acid (B4015-9 and B2351-20)



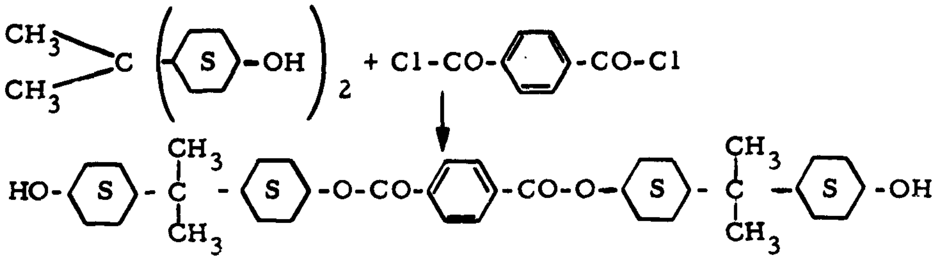
Ester of 2, 2-Bis(4-hydroxyphenyl)propane and SebacoylChloride (B2351-18)



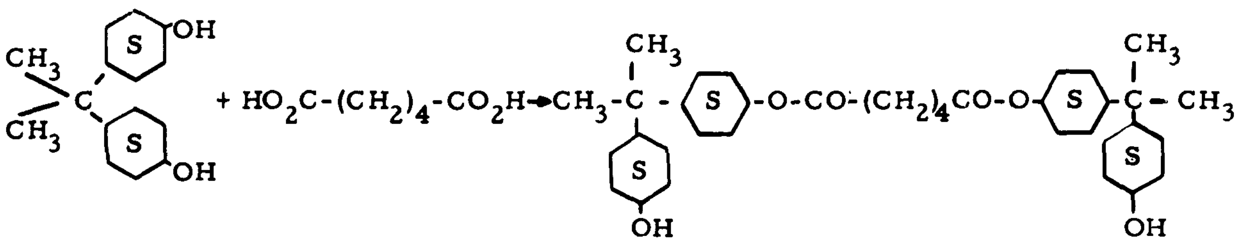
---

* (S) = Saturated ring structure

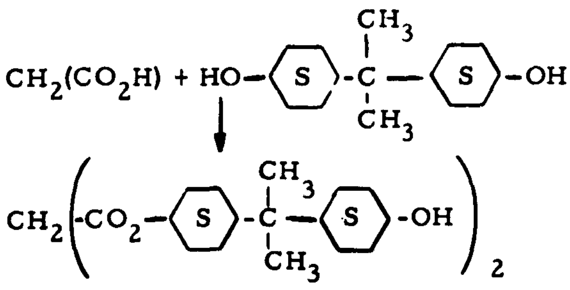
Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Terephthaloyl Chloride (B3615-41B)



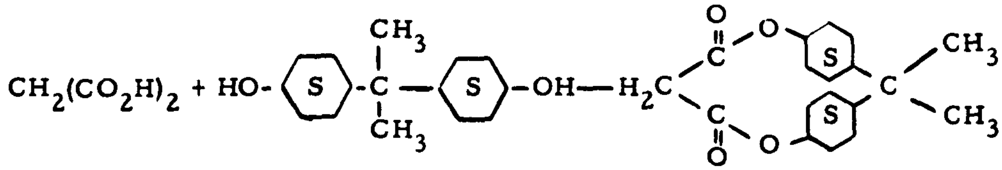
Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Adipic Acid (B3615-41A)



Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Malonic Acid (B2297-54)

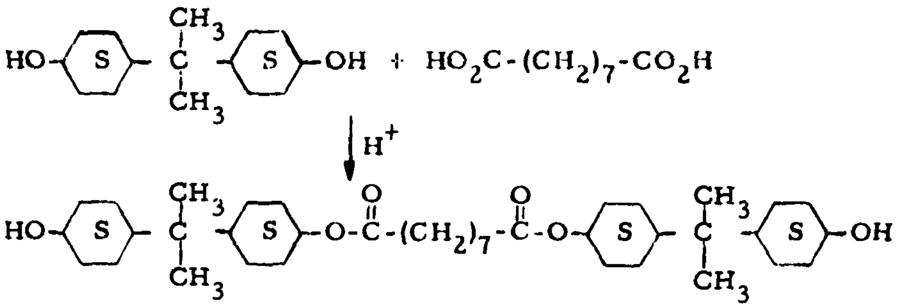


proposed course

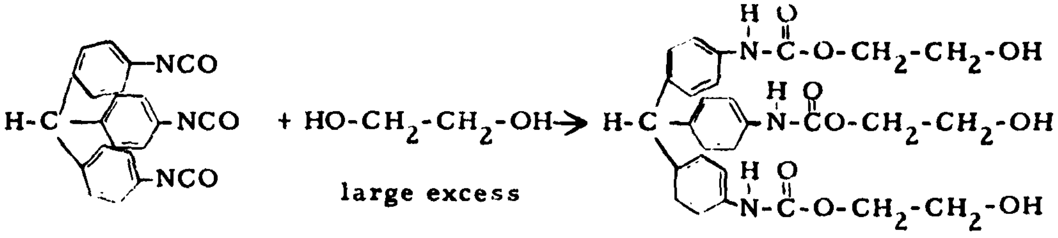


probable course

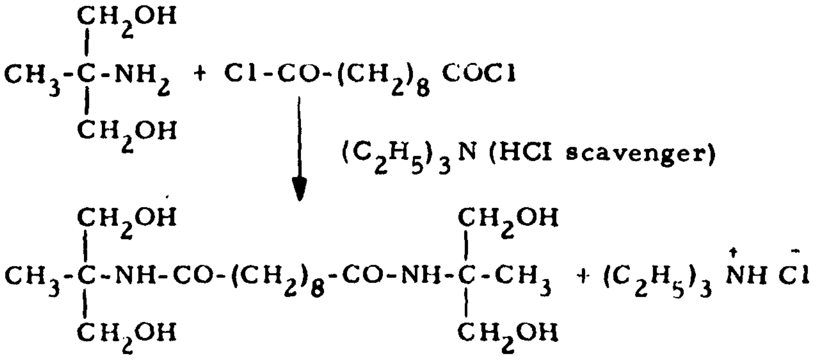
Ester of 2, 2-Bis(4-hydroxycyclohexyl)propane and Azeleic Acid (B2351-21)



Triol from Ethylene glycol with Triphenylmethane-p, p', p''-trisocyanate (B3615-39)



Tetrol from 1, 1-Bis(hydroxymethyl)aminoethane and Sebacoyl Chloride (B4015-11)



$$\begin{array}{c}CH_2OH\\|\\CH_3\text{-}C\text{-}NH_2\\|\\CH_2OH\end{array} + Cl\text{-}CO\text{-}(CH_2)_8\ COCl \xrightarrow{(C_2H_5)_3N\ \text{(HCl scavenger)}} \begin{array}{c}CH_2OH\\|\\CH_3\text{-}C\text{-}NH\text{-}CO\text{-}(CH_2)_8\text{-}CO\text{-}NH\text{-}C\text{-}CH_3\\|\\CH_2OH\end{array}\begin{array}{c}CH_2OH\\|\\ \\|\\CH_2OH\end{array} + (C_2H_5)_3\overset{+}{N}H\ \overset{-}{Cl}$$

A summary of the properties of those compounds whose syntheses were illustrated above is presented in Table VI.

Compounds	Physical State	Vapor Pressure Limitations at 10^{-2} mm Hg	Comments
Isocyanates			
B2297-43	Solid m.p. 170°C	None	M.P. too high
B2351-18B	Solid infusible	None	Too highly crosslinked
B2351-18C	Solid infusible	None	Too highly crosslinked
B2351-19B	Solid m.p.> 250°C	None	M.P. much too high
B4015-2	Solid m.p.> 250°C	None	M.P. much too high
B2297-48	Liquid	None	
B3615-46B	Solid m.p.> 200°C	None	M.P. too high
B3615-46A	Solid m.p. 120-130°C	High vapor pressure	M.P. somewhat too high - excess monomer boils on heating in vacuum
B3615-34	Solid m.p. 85°C	High vapor pressure	M.P. good but excess monomer boils in vacuum
Diols			
B3615-15	Liquid	None	—
B2297-47	—	—	Reaction failed to yield desired diol
B2297-49	—	—	Reaction failed to yield desired diol
B2297-51	Solid m.p. 150°C	None	M.P. somewhat too high
B3615-14	Liquid	None	—
B3615-40	Amorphous solid m.p. 50-55°C	—	Cyclized product obtained instead of diol
B2351-20	Amorphous solid m.p. 50-60°C	None	Active diol but yields friable foam
B2351-18	Viscous liquid	None	—
B3615-41B	Solid m.p. > 150°C	None	M.P. too high
B3615-41A	Viscous liquid	None	—

Table VI. Properties of newly prepared compounds.

Compounds	Physical State	Vapor Pressure Limitations at 10^{-2}mm Hg	Comments
Diols (continued)			
B2297-54	Amorphous solid	Volatile	Cyclized product formed instead of desired diol
B2351-21	Viscous liquid	None	—
B3615-39	Liquid		—
B4015-11	Solid m.p. 104°C	None	Cannot be purified by either recrystallization or distillation. Extremely H_2O soluble

Table VI. (continued)

From the above table it will be seen that none of the synthesized compounds was completely satisfactory for use in solid system vacuum foaming applications. The compounds were either liquids, excessively high melting solids, or tended to yield friable foams.

C. WATER SOURCES

At the start of the program it was theorized that one of the fundamental problems to be overcome was a source of water for CO_2 generation, since obviously water in the aqueous form could not be used in a one part storable system. One technique for introducing water in the system would be the use of inorganic salt hydrates, metal hydroxides and hydrated molecular sieves. With all of these sources heat could be used to liberate the water at the same time it was used to trigger the other foam components.

The type of test procedure set up was simply to mix the water bearing salt with an isocyanate and determine the rate of gas evolution at various temperatures, or the change in material viscosity with time. Tests in vacuum, however, were complicated by the vapor pressure of the isocyanate, so all preliminary tests were run in air.

Investigations with hydrates involved studies on the rate of gas evolution from mixtures of hydrates with toluene diisocyanate (5 ml) and triethylamine (0.5 ml). The amount of hydrate used was calculated to yield one equivalent of water per isocyanate. Results are tabulated in Table VII. The results shown in Table VII indicate that no gas evolution was detected with $MgO \cdot H_2O$ and $CaO \cdot H_2O$ with or without catalyst at room or at elevated temperatures. The $SiO_2 \cdot 1\text{-}1/2\ H_2O$ appeared to be too rapid at room temperature with catalyst and $(NH_2)\ C_2O_4$ and $BaCl_2$ both were too rapid under all conditions. The only material therefore which appeared promising was the H_3BO_3, which was therefore selected for further shelf life tests. Tests were not conducted with H_3BO_3 and TDI in vacuum because of the volatility of the TDI in vacuum, which would interfere with observation of gas evolution.

A second series of compounds, specifically metal hydroxides was investigated by determining the shelf life of mixtures of isocyanates with the hydroxides. Several of the hydrated metal oxides were commercially available whereas others required laboratory preparation. The compounds being investigated were chosen on the basis of their reported dehydration temperatures utilizing a range of materials dehydrating between 100° C and 300° C at normal pressures.

Mixtures of these hydrates with a commercial isocyanate prepolymer (Witco Fomrez P-420) were prepared and stored for 56 days at room temperature in small (2 oz.) screw top glass vials. The prepolymer was substituted for the TDI because it had a lower reactivity and volatility and it was also considered, by this time in the project, that such a material would have to be used in place of the TDI. Catalyst was omitted from these tests since initial tests indicated the reaction was too rapid when the free catalyst was incorporated in the mixture. It was therefore intended to use either encapsulated catalyst or catalyst incorporated in molecular sieves, which was to be procured at a later date. The samples were periodically visually checked for viscosity changes (polymerization). In the case of boric acid, aluminum hydroxide and calcium hydroxide, the amount of isocyanate was based on the theoretical amount of water formed during dehydration. For the lead and zinc hydroxides the amount required was calculated from their weight loss at 200°C. The results obtained are shown in Table VIII.

The results indicate that, from a standpoint of storage, boric acid, aluminum hydroxide, and zinc hydroxide might be suitable for use as a source of water in isocyanate formulations, whereas the other compounds would not be suitable.

Because boric acid seemed especially promising as a water source, a more refined rate study of its decomposition in the presence of a polyisocyanate (Witco Fomrez P-420) was carried out. The experiment was as follows:

Fomrez P-420 (5 gm) and boric acid (0.8 gm) were mixed in a small tube connected to a gas collection apparatus. The temperature was gradually raised and the volume of gas liberated was measured. Results of this experiment are illustrated in Figure 3 which demonstrates the rather sharp dehydration range of the compound. Boric acid also has the advantage of being capable of inhibiting prepolymerization by virtue of its acidic character.

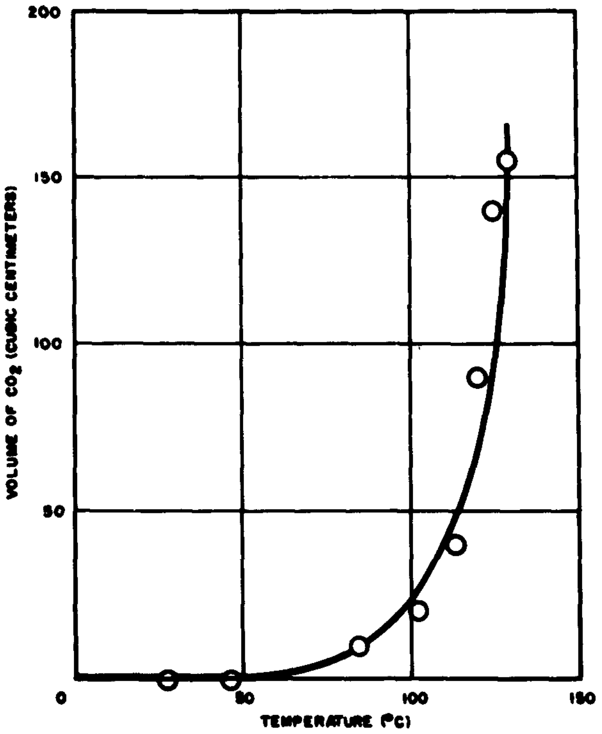


Figure 3. Rate curve for the liberation of water from boric acid (in presence of a polyisocyanate Witco Fomerez P420).

Hydrate (gms)	TDI* (gms)	Gas Evolution					
		Without Catalyst			With Triethylamine		
		25° C	100° C	150° C	25° C	100° C	150° C
$MgO \cdot H_2O$ (1.8)	6.6	None	None	None	None	—	None
$CaO \cdot H_2O$ (2.3)	6.6	None	None	None	None	—	None
$SiO_2 \cdot 1\text{-}1/2\ H_2O$ (1.8)	6.6	None	None	1CC/min	60CC/min	—	Very Rapid
$MnSO_4 \cdot H_2O$ (5.2)	6.6	None	None	None	None	—	None
H_3BO_3** (1.3)	6.6	None	None	30CC/min	None	40CC/min	None
$(NH_4)C_2O_4 \cdot H_2O$ (4.4)	6.6	2-3CC/min	Very Rapid	Very Rapid	Very Rapid	Very Rapid	Very Rapid
$BaCl_2 \cdot 2H_2O$ (7.6)	6.6	2CC/min	Very Rapid	Very Rapid	Very Rapid	Very Rapid	Very Rapid

* Toluene diisocyanate

** Without the presence of isocyanate, boric acid is reported to decompose at 185° C.

Table VII. Dehydration of hydrates in toluene diisocyanate.

Mixture Number	Inorganic Compound	Wt/5 gms of P-420 (gms) liquid	Effect of Room Temperature Storage For			
			8 Days	20 Days	43 Days	56 Days
101	H_3BO_3	0.79	No Change	No Change	No Change	Sl. Thicker
102	$Pb(OH)_2$	12.06	—	—	—	—
103	$Zn(OH)_2$	2.38	—	—	—	—
104	$Al(OH)_3$	1.01	No Change	No Change	No Change	No Change
105	$Ba(OH)_2 \cdot 8H_2O$	3.33	Hardened	—	—	—
106	$Ca(OH)_2$	1.43	Thicker	No Further Change	—	No Change
102A*	$Pb(OH)_2$	1.2	No Change	Sl. Thicker	Much Thicker	—
103A*	$Zn(OH)_2$	0.24	No Change	No Change	No Change	Sl. Thicker

* Mixtures 102A and 103A were prepared because 102 and 103 had such a high solids content that viscosity changes could not be noted.

Table VIII. Storage of hydrated metal oxides in the presence of isocyanates.

The relative ease with which molecular sieves release water when stored in the presence of isocyanates was also investigated. Initial studies utilizing Linde 4A and 5A molecular sieves showed that at 100 percent humidity and 25° C, Linde 4A can absorb 28. 1 percent water and Linde 5A can absorb 25. 6 percent water by weight. These moisture contents rapidly drop when removed from a 100-percent humidity environment. Vacuum drying of the saturated sieves at 100° C reduced the moisture content of 4A to 12. 7 percent and that of 5A to 11 percent. The partially dried samples then readily gained moisture on exposure to ambient conditions. Fresh samples of the sieves were then maintained in an ambient atmosphere until they absorbed various amounts of water. One-gram samples of the sieves were then mixed with 5-gram portions of a polyisocyanate (Witco Fomrez P-420). Each mixture was then sealed and set aside for shelf life determinations. The samples were periodically checked to determine the degree of change. Results are tabulated in Table IX.

Sieve	Water Content (%)	Effect of Room Temperature Storage				
		1 Day	4 Days	8 Days	14 Days	28 Days
Linde 4A	0 *	No Change	No Change	No Change	No Change	No Change
Linde 4A	3.7	No Change	No Change	No Change	No Change	No Change
Linde 4A	6.0	No Change	No Change	No Change	No Change	No Change
Linde 4A	11.1	No Change	No Change	No Change	Sl. Thcknd	Thickened
Linde 4A	19.9	No Change	Thickened	Hardened	—	—
Linde 5A	0*	No Change	No Change	No Change	No Change	No Change
Linde 5A	2.5	No Change	No Change	No Change	No Change	No Change
Linde 5A	4.0	No Change	No Change	No Change	No Change	No Change
Linde 5A	6.3	No Change	No Change	No Change	Sl. Thcknd	Thickened
Linde 5A	9.4	No Change	No Change	Sl. Thcknd	Thickened	No Further Change
Linde 5A	17.5	No Change	Thickened	Hardened	—	—

* Assuming sieves as received to be moisture free.

Table IX. Storage of hydrated molecular sieves in the presence of isocyanates

The above results indicate that, other things being equal, Linde 4A is somewhat superior to Linde 5A from the standpoint of moisture retention when stored at ambient pressures in the presence of an isocyanate. Linde 4A containing less than 7 percent absorbed moisture thus appeared suitable for compounding with isocyanates when stored at ambient pressures.

Efforts were then made to determine if such mixtures would react satisfactorily in a vacuum when triggered by heat. Regardless of the polyisocyanate being utilized, conclusive tests were difficult to obtain due to the high vapor pressure of the isocyanates themselves when heated in vacuum.

Mixtures of a commercial polyol (0. 1 eq.), p, p'-diphenylmethane diisocyanate (0. 1 eq.), 5-percent emulsifier, and 3-percent catalyst (8-hydroxy quinoline) with and without Linde 4A sieves (16 percent H_2O) were heated at 60 to 70°C in vacuum (0. 7 mm Hg). Vigorous bubbling occurred in both systems whether the sieves were present or not. This was taken as evidence that the bubbling was due mainly to the volatile isocyanate. Therefore in another experiment a sample of polyisocyanate prepolymer

(Witco Fomrez P-420, 3.94 gm) was devolatilized by heating in vacuum for 2 hours at 100° C. This resulted in a 38-percent weight loss. The gummy residue was then mixed with hydrated sieves (Linde 4A, 1.23 gm, 13.8 percent H_2O). Upon reheating at 70° C in vacuum (0.7 mm) the prepolymer melted and bubbles commenced demonstrating that sieves would release their water content. It was not known whether the bubbles were due to water vapor or to CO_2 formed from the reaction of water with the isocyanate. However, on continued heating no evidence of hardening appeared, which would have occurred due to urea and amide formation, if the water was reacting. Another experiment was performed in which hydrated sieves (Linde 4A, 0.5 gm, 13.8 percent H_2O) were also formulated with triphenylmethane-triisocyanate (1 gm) and heated in vacuum. In this system the sieves did not appear to liberate water until the triisocyanate had melted completely (between 155° C and 160° C). Two other experiments utilizing molecular sieves were carried out using a polyisocyanate prepolymer (Reichold 8625) which had been completely devolatized in a molecular still. Samples of the devolatilized prepolymer (1 gm) were then mixed with hydrated sieves (Linde 4A, 2.57 percent H_2O, 1.6 gm, and Linde 4A, 11.35 percent H_2O, 0.36 gm). Both mixtures began to foam when heated in vacuum (0.5 mm Hg) at 115 to 120° C even though the water content of the sieves varied significantly. On continued heating there was again no evidence of hardening, which was taken at the time, as evidence that there was little or no reaction between the water and the isocyanate. No further work was done with molecular sieves for this reason.

The conclusions from the work on water sources were that an inorganic salt, such as boric acid, might serve as a water source in an evacuated system. Molecular sieves, on the other hand, were believed to be unsatisfactory. Further consideration of the tests done, however, indicates that perhaps in the devolatilizing of the isocyanate prepolymers all the fast reacting components were removed, so that in a vacuum the water left the misture before reaction could take place. Unfortunately, no tests were run at atmospheric pressure to test this hypothesis. Also better results might have been secured if a fast acting catalyst had been included in the sieves; e.g., an amine catalyst on some sieves which would have been released with the water, thus forcing the reaction to take place faster. The use of sieves, therefore, for a delayed action foam cannot be said to be proved or disproved. Further work should be done on this concept.

D. ENCAPSULATION

Another method for making pre-mixed storable urethane mixtures involved the use of an encapsulation process. By use of this technique it was hoped that small discrete particles of isocyanate could be rendered nonreactive, and thereby put into intimate mixture with the polyol, and the other constituents. In an effort to find a source for encapsulating either liquid toluene diisocyanate (TDI) or solid diphenylmethane diisocyanate (MDI), all the known organizations doing this work were contacted. These included National Cash Register Company, Southwest Research Institute, Hollingshead Corporation and Rocketdyne Division of North American Aviation.

Negotiations with the National Cash Register Company resulted in a contract to provide twelve encapsulated isocyanate samples, of 100 gms each, having particle sizes of 100 to 500 microns, containing 60 to 80 percent of the active ingredient, 3,3' bitolylene 4,4' diisocyanate (TODI) and having release temperatures of 50 to 100°C. This order was later changed to include diphenylmethane diisocyanate.

Initial tests made of the encapsulated samples of MDI and TODI indicated that the TODI materials were not active enough. Of the samples containing 60 and 80 percent resin, the 80 percent samples were the best. Of the samples made with a 50°C and a 60°C melting encapsulant it was found that the 60°C materials were definitely superior with respect to resistance to damage while mixing and resistance to attack by a viscous polyol in preparing paste formulations. Consequently a larger quantity (3 pounds) of the 80 percent, 60°C encapsulated materials was ordered from the National Cash Register Company at a cost of $3200.00. In addition NCR offered to provide a small quantity of encapsulated CB-75, at no cost, when it appeared that this ingredient was vital.

Tests made using the larger quantities of materials were quite disappointing. It was not found possible to make satisfactory foams using the encapsulated MDI, as a direct substitute in formulations where pure MDI was found successful. The foams made were heavy (approximately 10-15 lb/cu. ft.) and of fairly low strength, possibly because of the plasticizing effect of the particular encapsulant used. The encapsulated materials did appear to be compatible with liquid polyols, without reaction for as long as three weeks, and did exotherm when triggered with heat, but the exotherm was not enough to sustain a reaction. These results then indicated that the concept of preventing reaction between the mixture of MDI and polyols by encapsulation was basically a sound one. However, to achieve a satisfactory foam additional efforts would have to be made to develop an encapsulant which is more compatible with the reacting and reacted materials. By the time these tests had been run concurrent tests, using other systems, showed so much promise that no further work was done on encapsulation.

E. CATALYSTS, BLOWING AGENTS, SURFACTANTS AND FILLERS

In the development of the powder formulations as each isocyanate-diol combination was tested it was necessary to make a great many tests with various catalysts, blowing agents and surfactants, (fillers were only tested on the most promising compounds). The catalysts, which were limited to solids, are shown in Table X .

Source	Designation	Type	Remarks
DuPont Co.	Moca	4, 4'methylene bis (2 chloro-aniline)	Slow acting
DuPont Co.	Caytur DA	Tertiary amine	Moderately fast Reputed inactive below 100°F
Houdry Process Corp	Dabco	triethylene-diamine	Very fast in MDI system
Metal and Thermit Co.	T-8	dibutyltin di-2 ethyl hexoate	Extremely fast in MDI system

Table X. Solid catalysts.

The blowing agents investigated fell into three classes: (1) those liberating water which reacted with the isocyanate to form CO_2 (only the best material previously found, boric acid, was tested here), (2) compounds which decomposed on heating to liberate nitrogen gas and (3) low melting, high vapor pressure compounds, such as MDI. A list of the materials tested, along with the results is shown in Table XI.

A number of surfactants were tested by incorporating small amounts (0.1 and 1 percent) of each surfactant in the same solid formulation. The effects of the surfactants were judged by cross-sectioning each sample and comparing it with a control made of the same formulation, however without surfactant. Uniform pore structure and freedom from large bubbles were the criteria for judging, and while all were somewhat equivalent in room temperature tests, considerable differences were noted when the tests were conducted under vacuum conditions. Unfortunately, the surfactants were tested in a formulation (25-9) which was later found to have very poor stability. This face undoubtedly played a part in the results secured. Because of time factors, however, it was decided not to repeat the tests, but a choice was made, which it is believed, resulted in the best material. The surfactant picked for subsequent tests was Union Carbide's L-521, a silicone-glycol copolymer. The list of surfactants tested is shown in Table XII.

A number of common filler materials including glass fibers, expanded silica, asbestos fibers, phenolic microballoons and wood flour were tried as fillers in a few formulations. These fillers were tried in two types of foams; those which frothed excessively in the vacuum and those which were too rubbery. It was hoped that the fillers would inhibit the frothing or strengthen the flexible materials. In no case was any improvement noted, and in all cases when over approximately 2-3 percent by weight was used the foaming action was definitely inhibited.

Class	Name	Formula	Decomposition		Remarks
			°C(760mm)	Product	
1	Boric Acid	H_3BO_3	300	$1\text{-}1/2H_2O$	Good at 760 mm and vacuum
1	Sodium Pyrophosphate	$Na_2P_207.\ 10H_2O$	94	$-H_2O$	Poor in vacuum
1	Sodium Phosphate Tribasic	$Na_3PO_4.\ 12H_2O$	100°	$-12H_2O$	Fair to poor in vacuum
1	Sodium Sulphate (Glauber's salt)	$Na_2SO_4.\ 10H_2O$	32.4	$-10H_2O$	Poor in vacuum
1	Oxalic Acid	$C_2O_4H_2.\ 2H_2O$	101	$-2H_2O$	Good at 760 mm in vacuum
2	U.S. Rubber Co. Celogen AZ	Azodicarbonamide	195-200		Poor under vacuum
2	DuPont Co. BL-353	N, N'dimethyl N. N' dinitrosoterephthalamide	105	N2	Poor under vacuum
3	Nacconate 300 (MDI)	diphenyl 4, 4'di-isocyanate	37°	--	Blows well under vacuum

Table XI. Blowing agents.

Source	Designation	Type
Applied Plastics	No. 353	Silicone
Atlas Chemical Co.	Tween 21	?
Antara Chemical Co.	Emulphor EL-719	Vegetable Oil
Dow-Corning Co.	No. 113	Silicone
Dow-Corning Co.	DC-200 (oils)	Dimethyl polysiloxane
General Elec. Co.	HF-1034	Silicone Glycol
Mobay Chem. Co.	Multron Additive No. 3	?
Union Carbide	L -520	Silicone Glycol
Union Carbide	L -521	Silicone Glycol

Table XII. Surfactants.

F. FOAMING POWDER DEVELOPMENT

The first foaming powder developed utilized readily available solid ingredients, which would react together, and was useful mainly in proving the general concepts; i. e., that the isocyanate and diol powders when mixed together in a stoichiometric ratio would have good storage life and could be melted together to form a polymer on heating. It also proved that foaming could be accomplished by liberation of chemically trapped water which, on heating, reacted with the isocyanate to produce CO_2 gas. This formulation, described previously which was labeled the "standard", is shown below:

Material	Function	Eq. Wt.	Eq. Used	Gm.
Diphenyl 4, 4'diisocyanate (Nacconate 300 - MDI)	Isocyanate	125	.05	6.2
Bisphenol A	Diol	114	.041	4.7
Pyrogallol	Crosslinker	42	.01	0.4
8-hydroxyquinoline	Catalyst		5% by wt	.55
Boric Acid	Water Source		5% by wt	.55
L-520 Silicone Glyrol (Union Carbide Co.)	Surfactant (pore size control)		1% by wt	3 drops

The above formula was found to be one which, when melted at 130-150°C at ambient pressures, resulted in a fairly low density, but very friable foam. Under vacuum conditions, however, excessive "boiling" and frothing occurred, so that it was impossible to obtain a usable product with this formulation. It was surmised that, at the temperatures required for melting, the vapor pressures of the isocyanate and the diol were far too high to be useful. Subsequent efforts were therefore concentrated on procurement of materials which would be more suitable for vacuum operation. These materials, which included solid isocyanate pre-polymers, solid diols and triols were either procured from commercial sources or synthesized at Hughes. The results of these investigations were detailed in a previous section. The first material which appeared promising was the solid pre-polymer prepared from an excess of a Mobay Polyester, Multron R-2, and the isocyanate p, p'-diphenylmethane diisocyanate, MDI.

With the development of this solid pre-polymer (designated MN-92) a polyol was available which, when reacted with the solid isocyanate (MDI) resulted in hard, tough polymer which foamed on addition of a water liberating agent. The polyester ingredient in the MN-92 had enough functionality so that a separate cross linking agent was not necessary. The formula for this foam powder, No. 13-2, is shown below:

Material	Function	Eq. Wt.	Eq. Used	Gms.
Diphenyl 4, 4'di-isocyanate (MDI)	Isocyanate	125	. 2	25. 0
MN-92	Diol and Crosslinker	200	. 25	50. 0
Boric Acid	Water Source		5% by wt	4. 0
L-520	Surfactant		3% by wt	. 25

This formula, 13-2, resulted in a tough, fine pored, non-friable foam of approximately 7-1/2 lb/cu. ft. density with a compressive strength of approximately 30 psi, when foamed at normal pressures in an oven set at 100°C. However, when the same formulation was reacted in a vacuum excessive bubbling and frothing occurred, which was almost as bad as the "standard" formula.

A large number of variations of the basic 13-2 formula were made in an attempt to improve the vacuum foaming characteristics. These variations included changing the isocyanate-polyol ratio and varying the blowing agent and/or surfactant proportions. In general varying the isocyanate-polyol ratio too much from the stoichiometric resulted in a poor polymer from a strength and a toughness standpoint. Variations in the blowing agent and surfactant resulted in many types of frothy foams which would either remain and cure as a mass of froth or would bubble up and then collapse, before curing. Attempts were also made to utilize catalysts to accelerate the curing rate and thus control the frothing. These too were fruitless since, because of the high reactivity of the MDI, the addition of even very small amounts of catalyst (. 001 percent to . 1 percent) would cause either extremely rapid polymerization, with little or no foaming, or a polymerized skin on top of the sample (approximately 10 gms), which, because of entrapped gas, would rise up to form a large hollow bubble, with very little foam inside.

As a result of the many experiments to improve the vacuum forming characteristics of the 13-2 formulation it was concluded that the use of the MDI as such would be unfeasible because of its high vapor pressure at the melting point of the mixture. Tests were consequently made to substitute TODI (3, 3' bitolylene 4, 4' diisocyanate-M. P. 73°C) for all or a portion of the MDI. Unfortunately, because of steric hindrance, TODI is a much slower acting material than MDI and it was not found possible to formulate satisfactory powders, even with the use of catalysts. The same results were found when DADI (dianisidine diisocyanate-M. P. 120°C) was substituted for all or part of the MDI in the 13-2 formula. Several-NCO-terminated glycols were synthesized without production of a satisfactory product. An -NCO terminated solid prepolymer was extracted from an ethyl acetate solution sold by Mobay Chemical Company. This material, designated CB-75, was isolated by vacuum evaporation of the solvent and was found to be reactive with the polyols being used.

The use of the CB-75 prepolymer as a replacement for part of the MDI in the 13-2 formula was found quite satisfactory since it had an M. P. of 105°C, with a consequently considerably lower vapor pressure than the MDI, at the foaming temperatures of 70-100°C. Because of its polyfunctionality the CB-75 also resulted in a more highly cross linked polymer when substituted for part of the MDI. The optimum formulation finally developed using the CB-75 is shown below, and was designated 25-9.*

The 25-9 formulation resulted in a 6 to 10 lb/cu. ft. density foam being prepared in vacuum. The material was as tough and non-friable

---

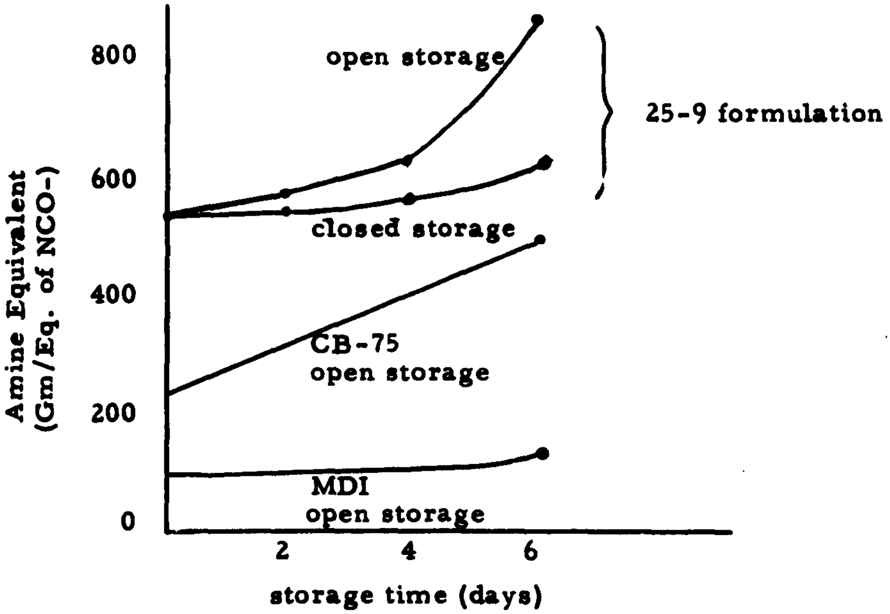
*An explanation of the formula numbering system is as follows: Individual formulations were numbered consecutively. However, whenever work was done on a number of variations of a basic formula a special report sheet was used. The formula was given the sheet number plus the dash number for the variation, i. e., 25-9 was the ninth variation on sheet 25. See appendix for examples of sheets.

Material	Function	Equivalents		
		Eq. Wt.	Used	Gms.
MDI	Isocyanate (high reactivity)	125 gms.	.05	6.3
CB-75	Isocyanate and cross linker	250 gms.	.2	50.0
MN-92	Diol	200 gms.	.31	6.3
Boric Acid	Blowing Agent	20 gms.	.45	9.0
L-520	Surfactant			1-1/2 gm.

as the previous 13-2 formulation, with the obvious advantage of being vacuum foamable. Samples as large as 6 inches in diameter and 6 inches high, with densities of approximately 10 lb. /cu. ft., were prepared at temperatures of approximately 150 to 250°F. While this material appeared to be distinctly superior to any formulation so far prepared several drawbacks were also noted. These were: (1) The minimum density obtainable appeared to be approximately 6 lb. /cu. ft. which was three times as high as desired. (2) The material in polymerizing appeared not to exotherm (probably because of the high percentage of prepolymer used). This then would limit the mass of material foamable, since if the reaction were endothermic the outer portions of the material would foam first and this would then insulate the inner mass from further heat. (This was borne out in tests of large masses). (3) The most serious drawback was the instability of the material whether confined or exposed to air. This instability resulted in little or no foaming in one to four days after mixing.

The instability problem was considered to be by far the most serious one concerned with the 25-9 formula. Consequently a number of tests were devised to determine the cause and a possible remedy. The tests which were run consisted of: (1) Preparation of a series of 25-9 formulations, each with one or two different ingredients missing, to attempt to isolate the malfunctioning ingredient. These were then checked at various intervals for change in apparent melting point (since a rise in the melting range was characteristic of the powder which would no longer foam). Another test consisted of adding "fresh" missing ingredients to the various partial formulations to determine which materials might be reacting together or which could cause foaming of aged partial mixtures. (2) Infrared spectra analysis of "fresh" and aged 25-9 formulations, and the separate ingredients and (3) amine equivalent determinations of "fresh" and aged 25-9 mixtures as well as MDI and CB-75 samples.

The results of the various tests clearly indicated that the CB-75 component was the major factor in causing the instability. It was found that CB-75 exposed to a laboratory atmosphere for as short a period as six hours changed in melting point from 100°C (approximately) to 140 to 160°C, and was also much less fluid at the higher M. P. than at the lower. Formulations made up without the CB-75 could be stored for a number of days with no apparent change, and on addition of "fresh" CB-75 satisfactory foaming took place, although not perfect, indicating some change in the MDI or MN-92 components. More quantitative data were obtained from the I-R and amine equivalent determinations. The I-R data clearly indicated changes within 46 hours in the -NCO and -CH bands which were found in the CB-75 component. See Figure 4. Similar tests run on mixtures of MDI, MN-92 and boric acid mixtures did not show these changes. Perhaps the most conclusive of the evidence against the CB-75 was found in the amine equivalent determinations shown below.



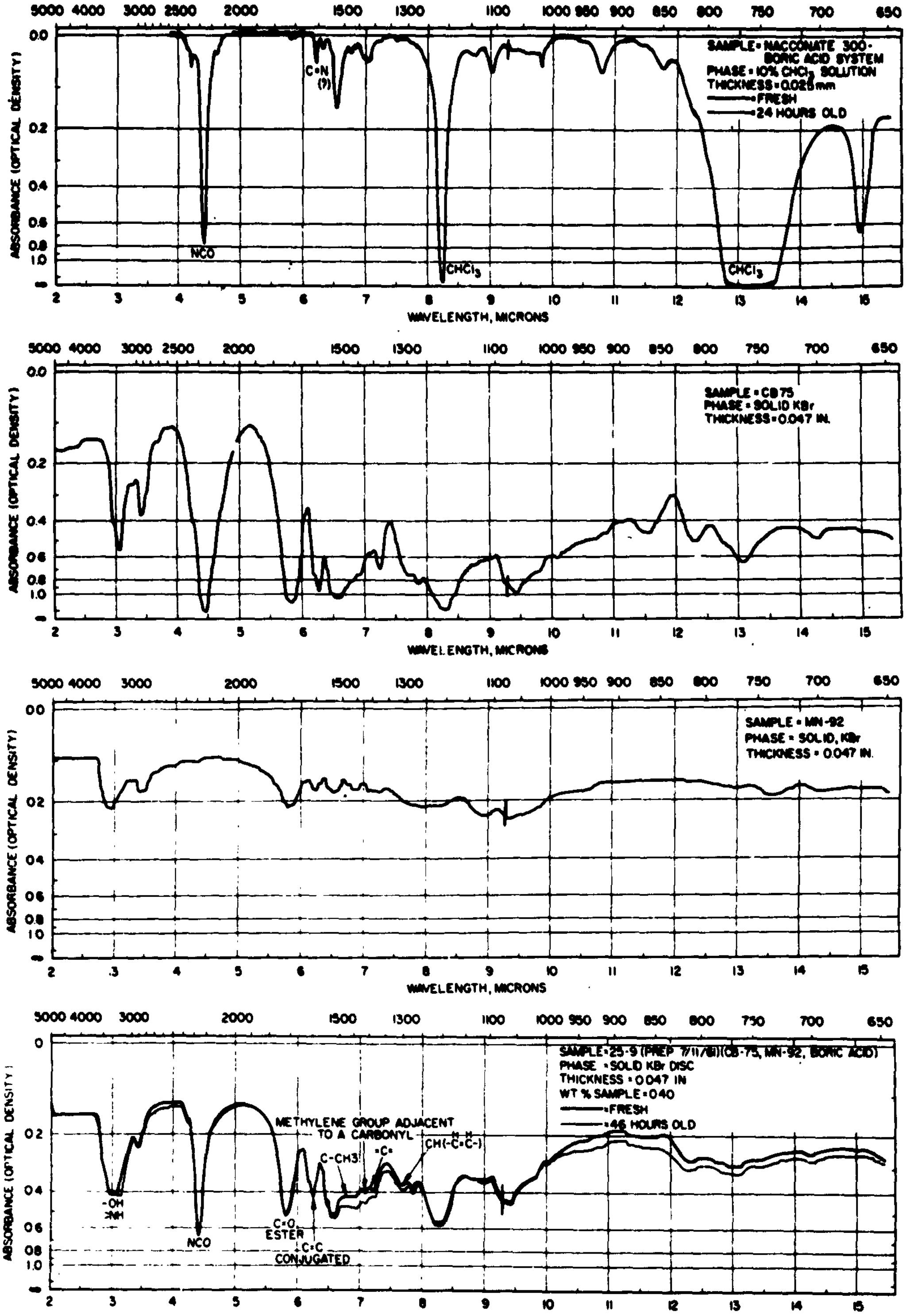


Figure 4. Infra-red spectrograms run on 25-9 formulation and individual components.

With the evidence of the instability of the 25-9 formulation it was decided to pursue two other paths, previously tried but not considered as promising as the "25" series formulations. These consisted of: (1) attempting to formulate powders using DADI (dianisidine diisocyanate) in place of the CB-75 and (2) utilization of Atlas G-1672 resin in place of the MN-92 in the 13-2 type of formula. Previous tests with this formulation had always resulted in a light frothy foam, somewhat similar to the 13-2 material foamed in vacuum.

Initial work was done utilizing DADI in place of the CB-75 and finally using trimethylol propane as an additional cross linker, oxalic acid as a blowing agent and T-8 as a catalyst. It was found possible to make foams ranging from 3 to 15 lb. /cu. ft. with the same formulation. A number of formulas, using variations in ratios of the above were tested, however, consistent results were not obtainable, and when it was found that 24 to 48 hours open storage would cause serious inhibition of foaming, this approach was dropped. A typical DADI-MDI-MN-92 formula is shown below:

Material	Function	Eq. Wt.	Eq. Used	Gm.
Dianisidine diisocyanate (DADI)	Isocyanate (slow reacting)	149	.1	15
Diphenyl 4,4'diisocyanate (MDI)	Isocyanate (fast reacting)	125	.02	2.5
MN-92	Diol	200	.06	12.0
Trimethylolpropane (TMP)	Cross linker	45	.08	3.6
Oxalic Acid	Water source			.02
Union Carbide L-521	Surfactant			.6
Metal and Thermit T-8	Catalyst			.05

Experiments with the MDI-G-1672 combination had previously been carried out using a small quantity (approximately 10 percent by molality) of pyrogallol as a cross-linker, but with the isocyanate-to-diol ratio approximately stoichiometric. As shown above, the addition of TMP in considerably larger quantities than theoretically needed for cross-linking, apparently resulted in a much superior product with the DADI based formulations. This approach was therefore taken in formulating the new series of tests using the two low molecular weight, low melting point diols available (Atlas Powder Company Isosorbide and G-1672), alone and in conjunction with MN-92, and using tris (hydroxymethylaminomethane) and trimethylol propane as cross-linkers and as a substantial portion of the polyol constituent. In addition the blowing agent was omitted, since it was found that the vapor pressures of the MDI and the diol were apparently high enough to cause foaming without an external agent. These foams were somewhat low in density (1-1/2 lb. /cu. ft.) and somewhat fragile, but it was believed they could be improved to be useful. The best formula (at that time), No. 185 is shown below:

	Eq. Wt.	Eq. Used	Gm.
Diphenyl 4, 4'diisocyanate (MDI)	125	.5	63
G-1672 (Atlas Chemical Co.)	166	.4	66.
Trisamino	40	.4	16.6
L-520			25

Additional work on optimization of formula #185 resulted in development of a somewhat similar formula, except trimethylol propane was used instead of trisamino for the cross-linker and the isocyanate-to-diol ratio was changed. The same diol was used as in #185, except procured from the Dow Chemical Company as resin X-2635. The Dow material, it was found, was more crystalline than that procured from Atlas Chemical. The foam produced from this formulation, designated #209, varied from 1-1/2 lb. density, made as small samples, to approximately 4 - 5 lb. when mad in larger masses. Some indication was found that as the material aged foaming was inhibited, but this tendency was not as pronounced as the 25-9 formulation. The formula for the 209 compound is shown below:

	Eq. Wt.	Eq. Used	Gm.
Diphenyl 4, 4'diisocyanate (MDI)	125	.144	18.0
X-2635 (Dow Chemical Co.) (ethylene oxide adduct of bisphenol-A)	166	.06	10.0
Trimethylol propane	45	.06	2.7
X-521 (surfactant)			1.0

Aging tests run on the 209 formulation gave erratic results, in that small samples two to three weeks old resulted in foams of 2 to 3 lb. density whereas batches of approximately 1 lb. in size resulted in foams of 2 to 5 lb. density. Heat rise tests, of small amounts, of fresh material made by burying a fine wire thermocouple in the foam powder, or pellet, gave definite indication of ar exotherm. The results of these tests are shown in Figure 5. It was planned to repeat the tests, using aged material, however, development of what appeared to be a more stable powder, based on DADI, caused cancellation of these tests.

Continuation of tests on the #209 formulation indicated that one cause for erratic results was reaction of the Union Carbide L-521 silicone-glycol surfactant with the MDI. Tests of reactivity of the various surfactants with pure MDI indicated that Dow-Corning 113 was the least reactive material, so it was used in all further tests. Additional tests made on several batches of #209 formulation indicated conclusively that the amine equivalent of the mixture increased noticeably both in the open and when maintained in closed storage. IR tests also indicated definite changes in the isocyanate component. After 3 to 4 weeks storage various batches gave foams ranging from 6 to approximately 20 lb/cu. ft. Because of these erratic results, and since the DADI base formulation appeared to have much better stability, further work was discontinued on this formulation.

Because of the early erratic results after short aging with the #209 formulation tests were made to attempt to substitute a less reactive

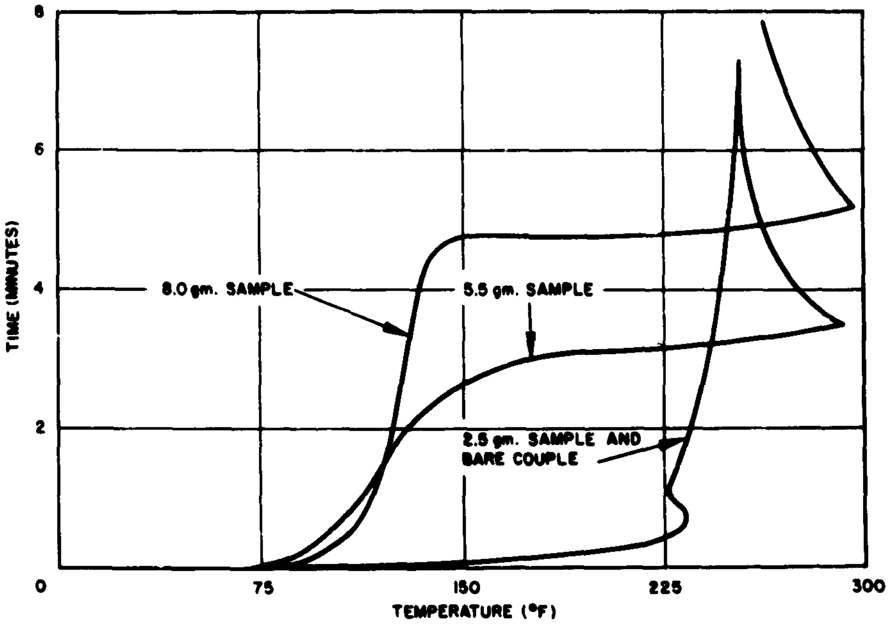
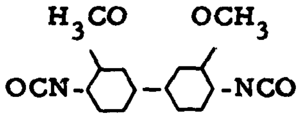
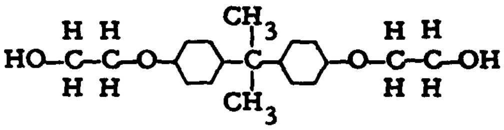
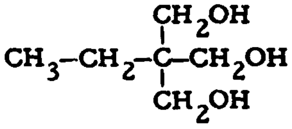


Figure 5. Exotherm curves No. 209 pellets (fresh).

isocyanate, dianisidine diisocyanate (DADI) or 3, 3' bitolylene diisocyanate (TODI) for the very reactive MDI. Direct substitutions, on an equimolar basis, did not prove successful since both materials apparently reacted too slowly. The powders would melt, a small amount of foaming would take place then collapse would ensue prior to setting up. Attempts were then made to catalyze the reaction to accelerate polymerization. Poor success was obtained with the TODI formulations, but a good formulation was developed with DADI based material. It was found that extremely small amounts of catalyst were required, so small that it was very difficult to add the catalyst directly to the mixture and get a uniform dispersion. The technique of making a 10X mixture was then adopted. This consisted of making a mixture containing ten times the required catalyst content. One part of this mixture was then mixed with nine parts of an uncatalyzed mixture, which could then be ground to a homogenous material. Using this procedure a number of mixtures were made in which the DADI was substituted in almost the same molal ratio as the MDI in the #209 formula, but with the addition of varying catalyst contents, from .001 to .2 percent by weight. The solid catalysts used included Metal and Thermit Corporation "T-8"; Houdry Corporation "Dabco", and DuPont Moca and Caytur DA. The mixtures with T-8 appeared to be the best, so efforts were concentrated on use of this catalyst. The most successful formulation, designated #67-3 is shown below:

Material	Function	Eq. Wt.	Eq. Used	Gm.
Dianisidine diisocyanate (DADI)	Isocyanate	149	.3	45.0
X-2635 Resin	Diol	158	.16	25.3
Trimethylol propane	Cross-linker	45	.15	6.8
DC-113	Surfactant		2.6% by wt	2.0
T-8 (dibutyltin di-2-ethylhexoate)	Catalyst		0.07% by wt	0.055

The sources for each ingredient, structural formulas, molecular and equivalent weights and melting points are shown below:

Material	Source	Mol. Wt.	Eq. Wt.	MP°C
Dianisidine diisocyanate (DADI)	The Carwin Co. North Haven, Conn.	296.27	149	120
Structural Formula	 DADI			
X-2635 p, p'bis (β hydroxyethoxy) 2, 2 diphenylpropane	The Dow Chemical Co., Midland, Mich.	316	158	102
Structural Formula	 X-2635			
Trimethylolpropane (TMP)	Celanese Chemical Co. New York City, N. Y.	134	45	58
Structural Formula	 $CH_3-CH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2OH$ TMP			
DC-113 Silicone-glycol copolymer (?)	Dow-Corning Corp Midland, Mich.			
T-8 dibutyl tin di-2-ethyl hexoate	Metal & Thermit Co. Rahway, N. J.			

As can be seen from the above the main ingredients came close to meeting the requirements set forth earlier; i. e., solids having a low molecular weight, and a M. P. of 50-80° C, (This melting point came closer to realization when it was learned how to pre-react the mixture).

The #67-3 formulation when heated in vacuum by infrared radiation commences foaming at a temperature of approximately 175°F and continues to expand and foam until approximately 350°F. Foaming becomes complete in approximately 2 to 5 minutes (depending on amount of material and temperature), and another 5 to 10 minutes at temperature is required to complete the cross-linking operation or dure. The foam produced is a good, tough, partially open celled material, non-friable,with a volume expansion ratio of approximately 20 to 40 and with density ranging from 2 to 5 lb./cu.ft. (The heavier densities are obtained when larger amounts are foamed.) Since this formulation showed very little evidence of an exotherm it was found that, because of heat input limitations, the maximum foam height obtainable was approximately 4 to 6 inches. This was nevertheless felt to be adequate for fabrication of the required structures, so further formulation efforts were ceased, except for a small number of tests to develop an ambient pressure foam. Physical property tests on the vacuum foamed material were also not performed, due to lack of time. Density determinations, however, were made, and storage tests of the unfoamed powder, stored open to the laboratory atmosphere so far indicate a life of at least two months. Effort was then directed towards development of production techniques to make large amounts of the foam powder, and to fabricate the required structures. Figure 6 shows a cross-section of the foam produced in a vacuum atmosphere.

G. PRODUCTION TECHNIQUES

In the preparation of laboratory samples small amounts of powder were hand mixed, ground in a mortar and pestle and finally sized by being put through a 40 mesh sieve. Using these techniques several hundred grams could be uniformly prepared in a few hours. However, with the development of the initially successful #25-9 formula and the later #67-3 formula it then became necessary to devise methods of producing large quantities of the powder using mechanical, production techniques.

Since the DADI was supplied as a fairly fine, brittle powder it was found relatively easy to reduce this material to a 40 mesh by a simple ball milling operation. This mesh size appeared to be the largest in which a powder could be intimately mixed to give a good reaction. The X-2635 diol and the trimethyol propane, however, were both materials with lower melting points, and were not hard crystals or brittle, but rather inclined to gumminess when ground. Attempts to mix and grind these materials, with the isocyanate and the other components, were made using a ball mill, a drug mill, a Cumberland granulator and a counter current muller type mixer. In every case "gumming" up occurred, with very little production of a homogeneously mixed powder. Grinding the diol and triol individually

Figure 6. Cross section of No. 67-3 formula.

to 40 mesh size, and then mixing was found almost as slow. The method finally adopted consisted of running the TMP through a hand operated meat grinder, then sieving through a 30 mesh screen. The X-2635 resin was first thoroughly chilled with dry ice, to embrittle the crystals and then, still mixed with dry ice, was ground in the Cumberland granulator. It too was sieved through a 30 mesh screen. All the ingredients, in the correct proportions, were then preliminarily mixed in a Hobart single paddle mixer to obtain a resonably good mix. This mixture was then run through a small kneading type (sigma blade) mixer and "worked" until definite evidence of pastiness was observed in the mix. This pastiness was also accompanied by a temperature rise. When the temperature reached 40 - 45°C the paste was removed and allowed to cool. After cooling the material was brittle enough so it could easily be run through the granulator to produce a fine, homogeneous powder which would pass through a 30 mesh screen. Other methods of obtaining the powder might also be developed, such as grinding in liquid nitrogen, however, they were not tried due to lack of time and because the method finally developed appeared the simplest. In the limited tests which were run there appeared to be no difference in the reaction rate of the pre-reacted powder and material which was mixed without the pre-reaction.

In fabricating the chair it was assumed that the material could be used as a powder, however, for use with the balloon it was necessary that the material be in a form which could be easily attached to the inflated skin. Experiments with the powder in a small press die indicated that the material could be satisfactorily pelletized, at room temperature, using pressures of 1000 - 2000 psi. Additional tests indicated that these pellets could be satisfactorily made at high speed in a conventional plastic automatic pre-forming press. Attachment of the pellets to the balloon skin was at first tried by heat sealing, but it was found that the pellets would drop off from vertical surfaces when heated during the foaming operation. Further tests then established that the pellets could be satisfactorily adhered to the skin by means of Goodyear "Pliobond" rubber cement.

IV. STRUCTURES DEVELOPMENT

A. PRELIMINARY STRUCTURES TESTS AT HUGHES AIRCRAFT

1. Chair Fabrication

In the fabrication of the chair it was decided that, in order to meet the requirement of a completely vented mold, the mold should be made of 1/2 inch mesh wire screen (hardware cloth), lined on the bottom and sides with mylar or Dacron fabric as a parting film. Figure 7 shows the type of mold constructed. Prior to working with the full sized mold, however, a 1 foot cube of hardware cloth was made so that semi-full scale tests could be run, using small amounts of material, Since it had already been found impossible to foam up the full 12 inches in height, in tests in the belljar, provisions were made to put shelves in the cube so that layers 3, 4, or 5 inches high could be foamed. It was thus hoped that the optimum foaming height could be determined and also to determine if by foaming several layers simultaneously they could be made to join one another to form a solid monolithic block.

Using the cube then a number of preliminary tests were made, first with the original #25-9 formula and later with the more successful #67-3 formulation. Tests which were made consisted of using varied amounts of powder, to determine the optimum amounts, the effect of varied heating rates, final cure temperatures, etc. The tests were all conducted in an altitude chamber at pressures corresponding to 160,000 ft altitude. In all tests the chamber pressure was reduced to approximately 2 mm. Hg before heat was applied. Heating, initially was supplied using the chamber walls, which could be heated to approximately 700°F in approximately 30 minutes. This rate of heating caused foaming to commence in approximately 20 minutes after heat was initiated. This heating rate was found to be too slow for optimum foaming so later tests utilized General Electric T-3 1 kw, 220 volt quartz infrared heating lamps. The one foot cube was, in later tests, heated by 6 such lamp banks, each bank holding 5 lamps. Figure 8 shows the cube mold as suspended in the chamber, with a layer of powder on each shelf, just prior to foaming. In the test shown it was planned to test the ability of

Figure 7. Hardware cloth chair mold coated on inside with 1 mil mylar film.

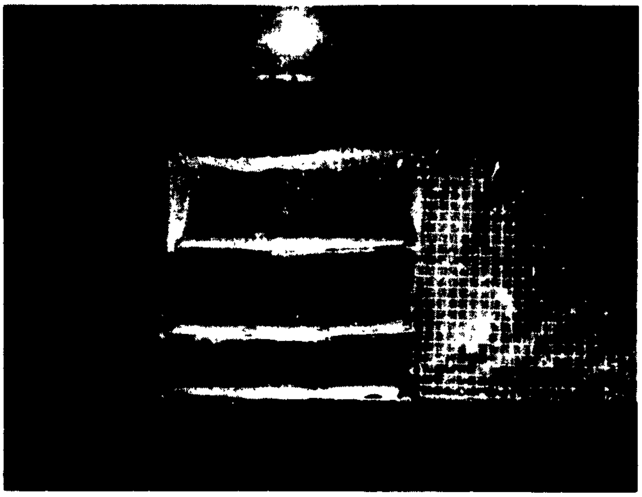


Figure 8. One-foot cube mold with No. 67-3 powder just prior to foaming.

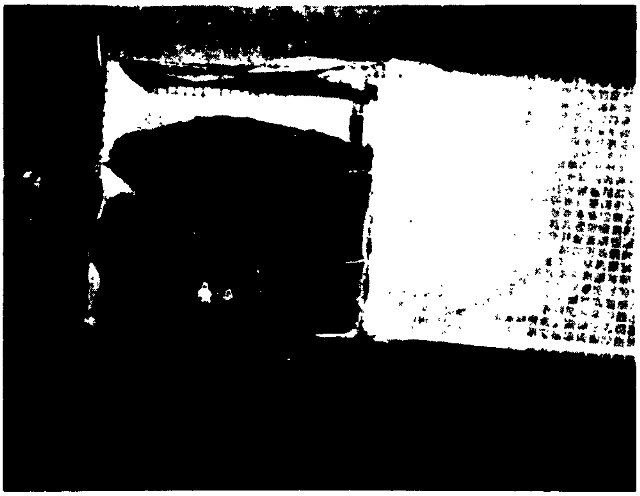


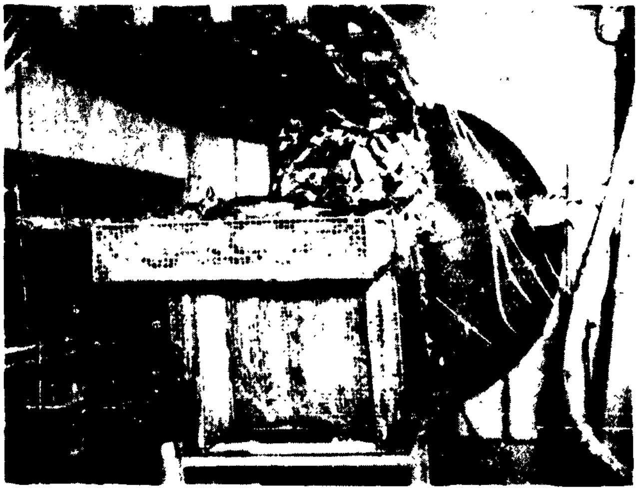
Figure 9. Cube mold with No. 67-3 material foamed with 3-, 4-, and 5-inch separators.

the powder to foam up 3, 4, or 5 inches in height. The amount of material on each shelf was calculated to yield a foam at approximately 4 lb/cu ft. density, if full expansion was realized. Figure 9 shows the results of foaming the material shown in Figure 8. It should be noted that the 3 and 4 inch thick layers apparently foamed up almost the complete height, whereas the 5 inch layer foamed less than each of the others. The reason for this anomalous behavior was apparently that the layer to be foamed 5 inches was thicker than the others and thereby took more heat to foam completely. Unfortunately since the top layers of powder (on the 5 inch shelf) foamed first this reduced the heat which reached the lower layers. The top layers therefore foamed and "set" completely before the lower layers commenced to foam, thus inhibiting any foam formation by the lower layers.

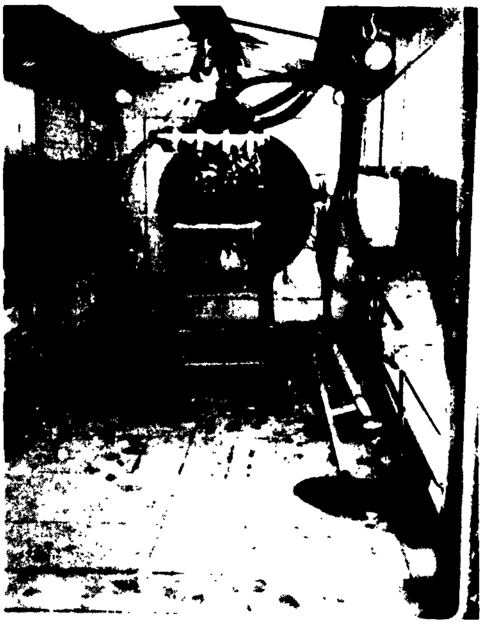
The results of a number of such tests indicated conclusively that: (1) the maximum height of foaming which could be expected from this type of formulation was approximately 4 inches. (2) Heat should be applied rapidly at first, then turned down during the "setting phase, (3) It would probably not be possible to cause layers to foam simultaneously on separate shelves and then join together to form one large block.

With the knowledge gained in the cube tests, it was decided that the full sized chair could be made, however, using a somewhat different procedure than employed for the cube. Heating would be done entirely by use of quartz lamps, so the heat could be rapidly applied, and conversely rapidly diminished. It was also decided that the large block would be made by multiple "blows," i. e., by foaming up a quantity of material to its maximum, cooling the foam then adding more material on top of the solidified foam (tests indicated that the two layers would bond together excellently), reheating, etc. It was also decided that the easiest way to form the large block, without foaming up the narrow arms, would be to have the mold lying on one side. Foaming would be started from the center, using a shelf, which later was removed when the mold was turned over to foam the other half of the chair. (See also Figures 23 through 27.) While this procedure would undoubtedly be more time consuming, it had the definite advantage of being certain. Figure 10 shows the set-up utilized for production of the chair at Hughes. The lampbank consisted of 140 lamps, arranged in 20 sections of 5 lamps each above the mold and 20 lamps on each side of the mold, with aluminum foil on each end for reflectivity. The lamps (nominal operating voltage 220 volts) were operated at 60 to 90 volts for the first 2 to 4 minutes until foaming was definitely in progress, then turned down to 30 to 60 volts as the material set. Imbedded thermocouples indicated temperatures as high as 450°F at the top surface of the foam or just above the foam and, at the end of approximately 15 minutes, approximately 180°F at the bottom. Interestingly enough when the heat was turned off after approximately 20 minutes of heat application, to reach the above temperatures, the upper thermocouple showed an immediate drop, whereas the inner couple frequently rose to as high as 300°F. These temperatures, of course, varied from test to test, depending on the exact location of the thermocouples with relation to the lamps, the amount of foam covering the thermocouples, the lamp distance from the foam, etc. With the limited number of tests run then it was not possible to develop a technique for using the thermocouples for process control. However, it is believed this could be done by a series of standardized tests.

Using the procedure outlined above the two chairs shown in Figures 11 and 12 were made at Hughes, at a pressure corresponding to 90,000 ft altitude. The chair shown in Figure 11 was the first chair while that in Figure 12 was the second chair made. The difference was the result of using only powder in the first chair, whereas both powder, small pellets and large 13 inch diameter 3/16-inch thick pellets were used in the second chair. The use of the large pellets, it was found, resulted in a considerable advantage in placement of material, particularly in adding material to previously blown, unevenly surfaced foam. Another technique which aided considerably in filling out the square contours of the chair was the incorporation of small pellets adhered to the sides of the mold. During foaming the pellets on the side would foam and fill in the depressions on the sides of the large foam



(a)



(b)

Figure 10. Set-up used for producing first foamed chairs at HAC.

Figure 11. First foamed chair made at HAC. Foamed at 90,000 feet.

Figure 12. Second foamed chair made at HAC. Foamed at 90,000 feet. Special techniques utilized to effect improvements.

mass. (The large amount of foam would tend to rise as a sphere, rather than following the mold contours, because of lack of back pressure.) The differences in the two chairs illustrate the effectiveness of the special techniques.

2. Balloon Fabrication

Concurrently with development of the process for fabricating the chair, tests were made to determine the optimum fabricating techniques for production of the inflatable structure. With the development of the pellet concept and the technique for adhering them to the balloon skin it was then necessary to determine the optimum pellet size, spacing, method of heating, etc., just as in the case of the chair.

Somewhat analogous to the use of the one foot cube mold it was decided to construct a 2 foot diameter sphere to be utilized in determining the optimum processing techniques. For the skin a Hypalon coated nylon fabric was obtained from the E. I. DuPont de Nemours Co. This material, DuPont #72-010 was selected for its ready availability, its light weight, 8.0 oz/sq yd, and good heat resistance. An eight gored balloon was constructed, double sewing each gore in a simple overlap seam. A one inch wide strip of the same fabric was cemented to each seam on the interior to act as a seal.

Previous tests on small flat samples indicated that 2-3/8 inch diameter pellets, approximately 3/32 inch thick, containing 6-1/2 to 7 grams of resin, would give a 1 to 1-1/2 inch foam if placed as closely as possible on the skin. It was planned to use the same type of quartz lamps, for heating as were being used in the chair tests. Initial tests, on vertical sections, had indicated that some restraint was required on the pellets to prevent flowing, as the material liquified, just prior to foaming. The method finally devised to furnish the restraint was to heat seal a light, highly wrinkled, Dacron marquisette fabric, to each pellet, using a heated sealing iron and the thermoplastic properties of the pellets to affect the seal. (The large amount of wrinkles in the fabric were to allow room for expansion.) The Dacron fabric was a special marquisette (similar to curtain cloth), having a weight of .65 oz per sq yd and a mesh of 33 x 38 to the inch, made by Stern & Stern fabrics as #15462.

The set-up for rigidizing the 2-foot balloon is shown in Figure 13 and Figure 14 shows the results of the process. From these tests it was found, by the use of fine wire thermocouples, that foaming commenced at approximately 170°F and continued for approximately 5 minutes until a temperature of approximately 250°F was reached. A cross section of the balloon after rigidization is shown in Figure 15. The temperatures are considered approximate in this, and in the other readings cited, since the temperature indication was very dependent on the placement of the thermocouple with respect to the lamps, the amount of powder covering the couple, the extent of foam, etc. The figures were borne out to some extent, however, by tests of very small amounts on a melting point apparatus. Identical figures were not obtained because of the difference in heating methods and pressures during foaming.

The method of construction of the 2-foot balloon indicated that the fundamental concept was sound. Therefore a full size (7-foot diameter) balloon was ordered built in accordance with HAC print 27D-19204. The balloon was constructed by the Aeroleather Corp. of Los Angeles, using the same general construction methods as were used on the 2-foot balloon. The large balloon was covered with pellets and heat sealed to the loose Dacron similar to the small structure. Figure 16 shows the balloon prior to coating with pellets. Figure 17 illustrates the method of application of the pellets to the balloon surface. Figure 18 shows the balloon after application of the pellets and Figure 19 shows the appearance after the heat sealing operation. Figure 20 is an approximately full scale closeup of the pellets, prior to heat sealing. (Note the good adherence despite numerous cracks.) Figure 21 is a closeup after the heat sealing operation. Figure 22 shows the balloon crated for shipment to WPAFB. The crated balloon, folded similar to a football bladder, was approximately 10 feet long and weighed approximately 55 pounds.

B. DEMONSTRATION AT WRIGHT-PATTERSON AIR FORCE BASE

The production of the chair at WPAFB was very similar to the process carried out at Hughes Aircraft, except that the chamber pressure was somewhat lower, approximately 1 mm Hg, corresponding to 150,000 ft altitude.

A lesser number of lamps were used, 84, and voltages ranged from 30 to 90. Temperatures were recorded from 150°F to 350°F, depending on the particular thermocouple location. The chair was made in seven stages, six for the bottom and arms and one for the back. Heating each additional powder and pellet load to the foaming temperature, and to "set" took approximately 15 - 20 minutes, however, bringing the chamber to altitude, cooling the foam prior to pressurization, and then adding the new material made each stage take approximately 2 hours. Figures 23 to 29 illustrate the steps required in fabricating the chair. The final weight was 44 pounds for the approximately 10 cu. ft. in the chair.

Fabricating the inflated structure was likewise very similar to the operation at Hughes, once the lamps were arranged so that even heating was accomplished. The arrangement for inflating the balloon and controlling the balloon pressure during the "ascent," rigidization and cooling is diagrammatically shown in Figure 30. After the balloon had been brought to altitude a constant internal pressure of 5 inches of water was maintained all during the rigidization process.

Rigidization was accomplished by heating the balloon as uniformly as possible with the lampbank shown in Figure 32. The lampbank consisted of three sections, each individually controlled by a variable voltage source. During rigidization voltages varied from approximately 30 to 75 volts. Variation of the voltage was determined by observation of the foaming process. In order to adequately heat the balloon it was rotated approximately 16 degrees (or 1 foot on the "equator") every 12 minutes. Because of non-uniform heating, it was not possible to adhere accurately to this schedule. After approximately 4 hours the balloon was completely "cured," and the pressure was restored to ground level. A hole was cut in the rigidized skin to enable the depth of foaming to be ascertained. The foamed structure ranged from 1 to 1-1/2 inches in thickness and the structure supported itself very well when either suspended from the attachment hook, or when resting on the ground. Figures 33a and 33b show some of the steps in fabricating the rigidized structure. The finished structure, which weighed approximately 50 pounds, is shown in Figures 34 and 35.

It should be noted that when the structure was "brought down to earth" there was very little evidence of either distortion of delamination, which might have occurred on release of tension in the skin material. Another condition, never previously seen, was the large number of external "bubbles" which appeared on the surface area first exposed to heat, as contrasted to those areas heated several hours later. It is theorized that the "bubbles" were caused by occluded air which was expanded when the heat was first applied. Later on, as the chamber warmed up, and the air was removed by the vacuum and heat, the surface after rigidization was relatively smooth, except for some spots due to breaks in the Dacron restrainer cloth. This condition is shown by the many bubbles shown in Figure 35 just above and to the right of the center of the hole. This area was heated first. To the left of the center was the area heated last.

Figure 13. Two-foot diameter test balloon just prior to heat application. Note arrangement of pellets and lamps.

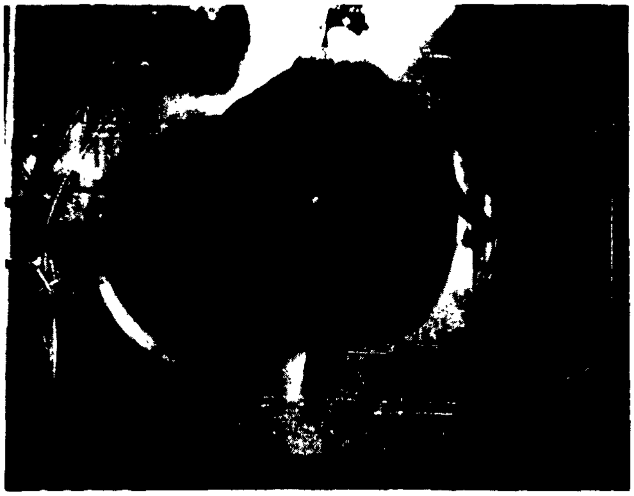


Figure 14. Test balloon after heat application. Note loss of adhesion of Dacron restrainer cloth.

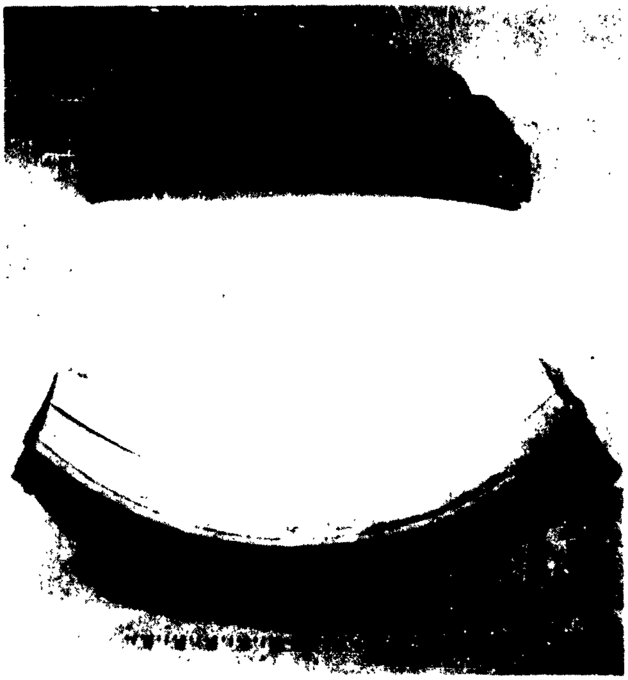


Figure 15. Cross section of two-foot balloon after rigidization.

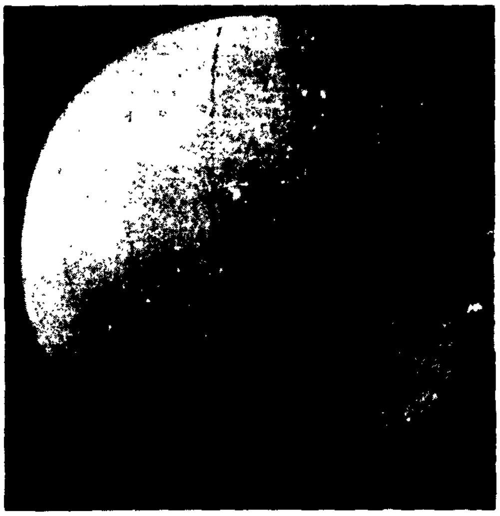


Figure 16. Seven-foot diameter balloon prior to application of pellets.

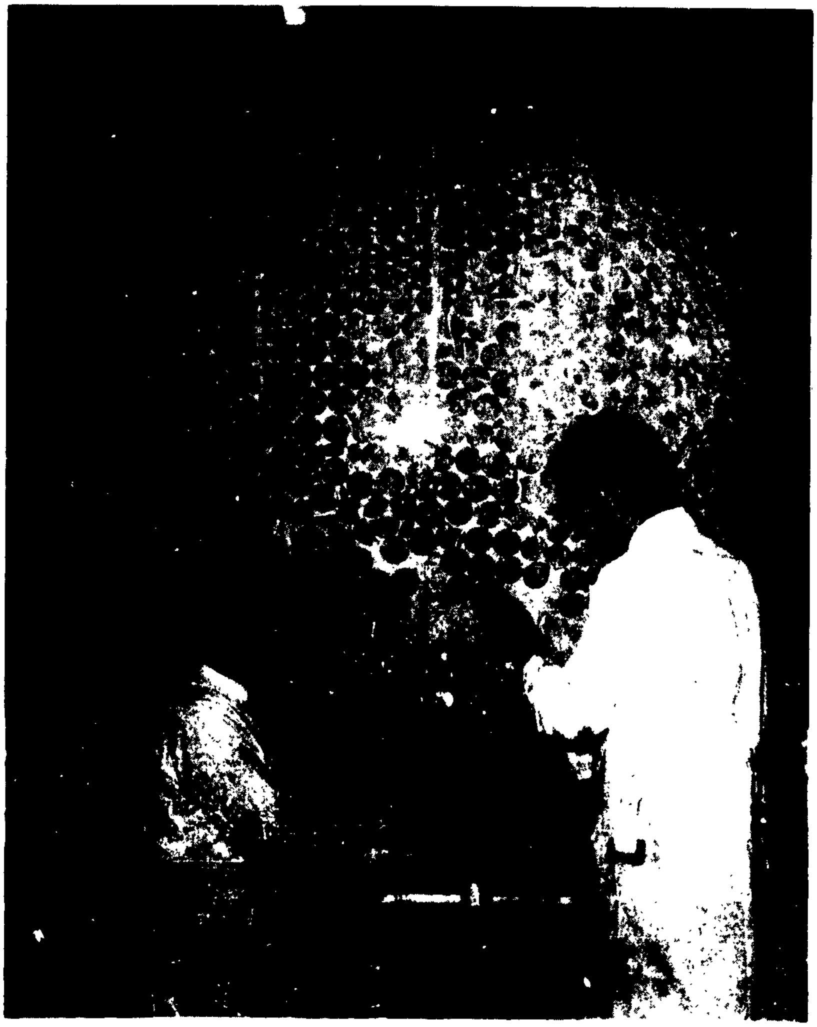


Figure 17. Application of rubber cement coated pellets to cement coated balloon.

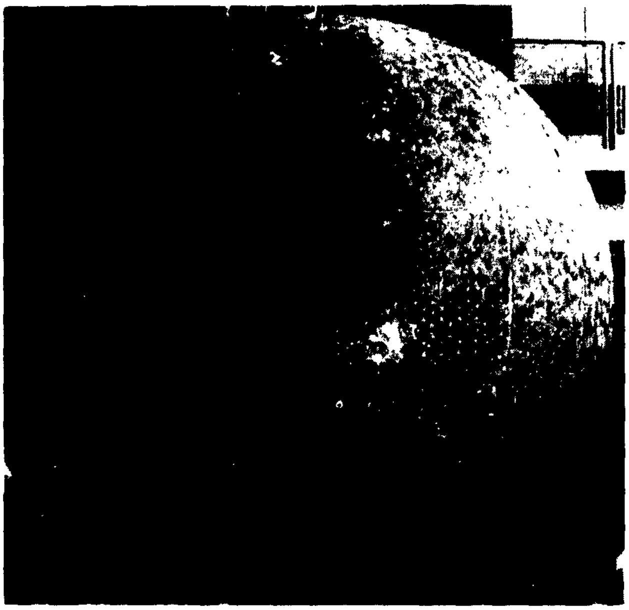


Figure 18. Seven-foot diameter balloon after application of approximately 4500 pellets.

Figure 19. Appearance of balloon after heat sealing Dacron restrainer cloth.

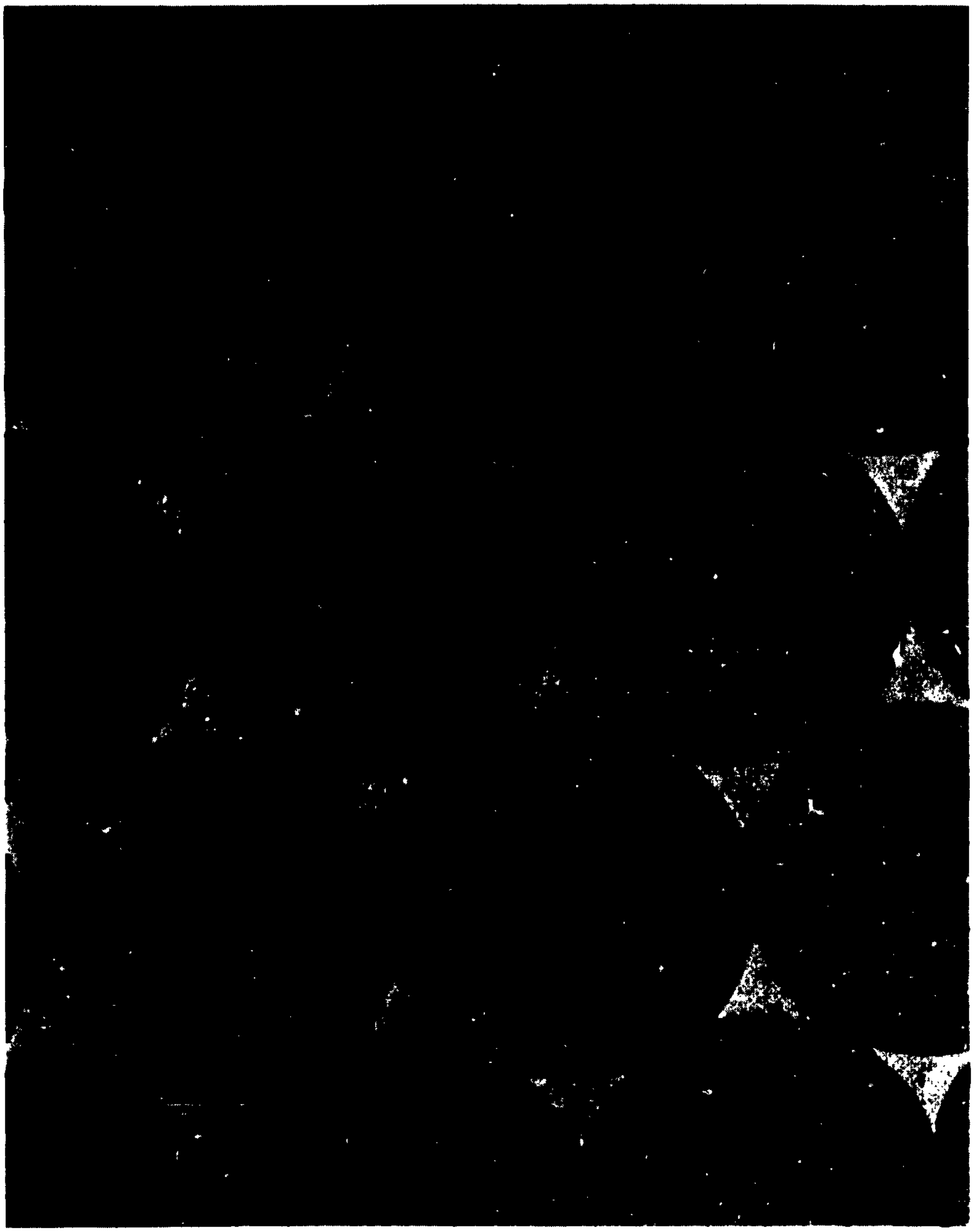


Figure 20. Full-scale view of pellets cemented to balloon skin. Note excellent adhesion despite numerous cracks in pellets.

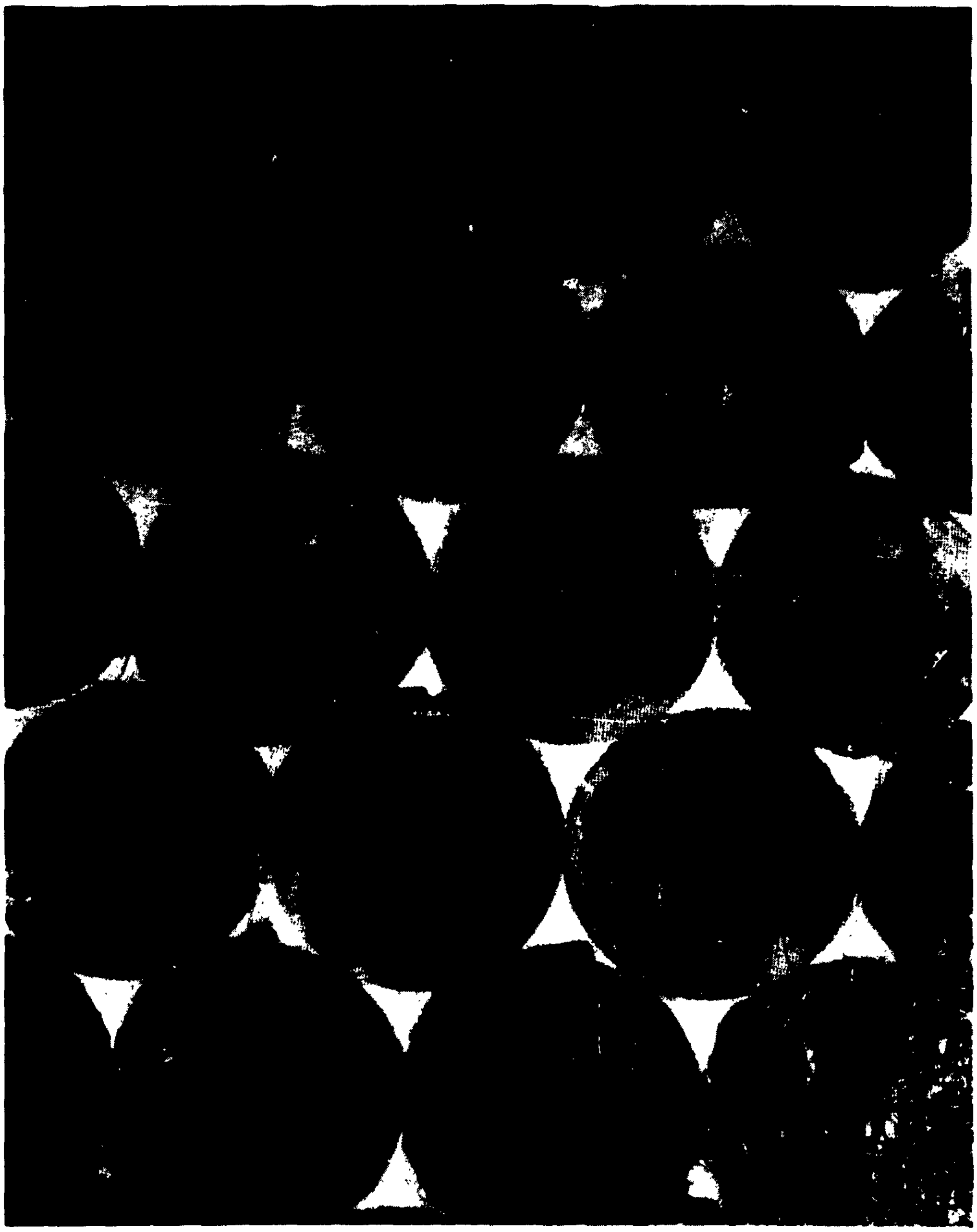


Figure 21. Typical appearance of balloon surface after heat sealing the Dacron restrainer fabric.

Figure 22. Balloon crated for shipment to WPAFB.

Figure 23. Chair mold in position prior to foaming first load. Note use of powder on center shelf and pellets on sides. USAF/ASD photo.

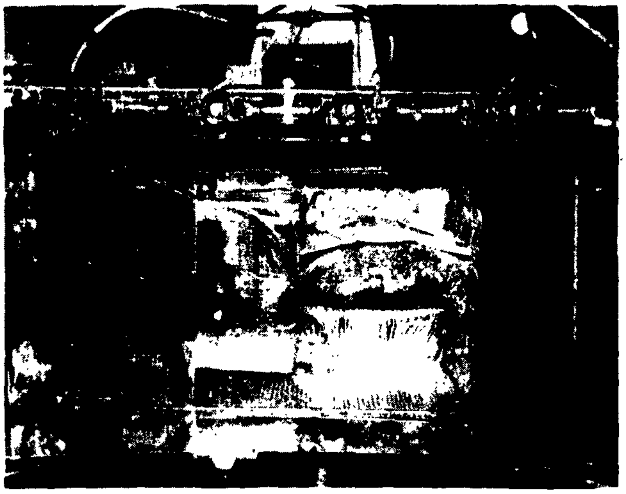


Figure 24. Appearance of foam after first "blow." Material in place for second "blow," note use of large pellets on surface of foam.

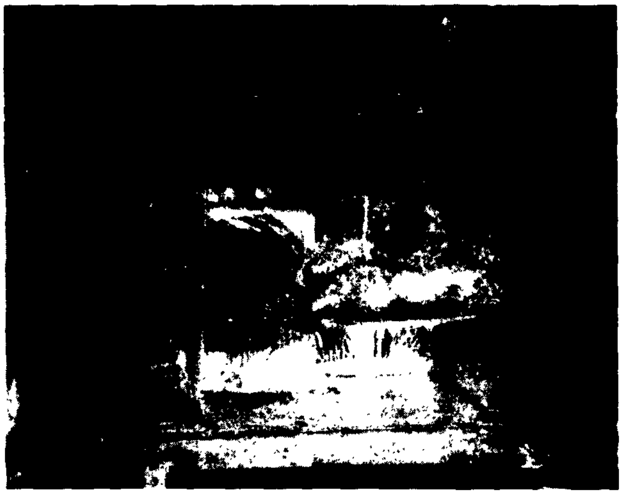


Figure 25. Appearance of foam after second "blow." Material in place for third "blow."

Figure 26. Appearance after third "blow." Mold has been turned over, the shelf has been removed, and additional large pellets are in position for fourth "blow."

Figure 27. Appearance after sixth "blow." Chair now ready for final foam application to back. USAF/ASD photo.

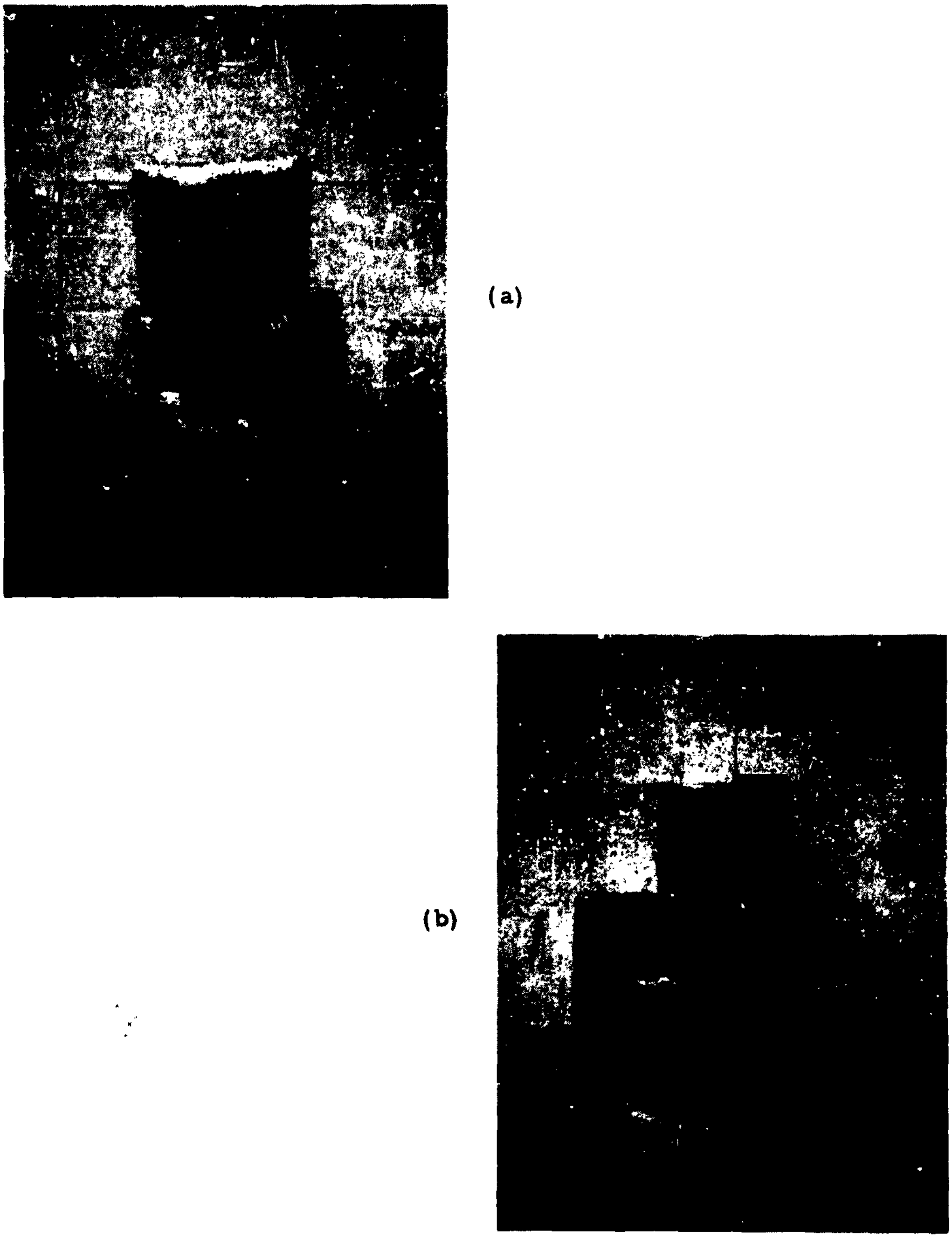


Figure 28. Views of completed chair. Back was completed in one "blow."

Figure 29. Illustrating structural capabilities of foamed chair.

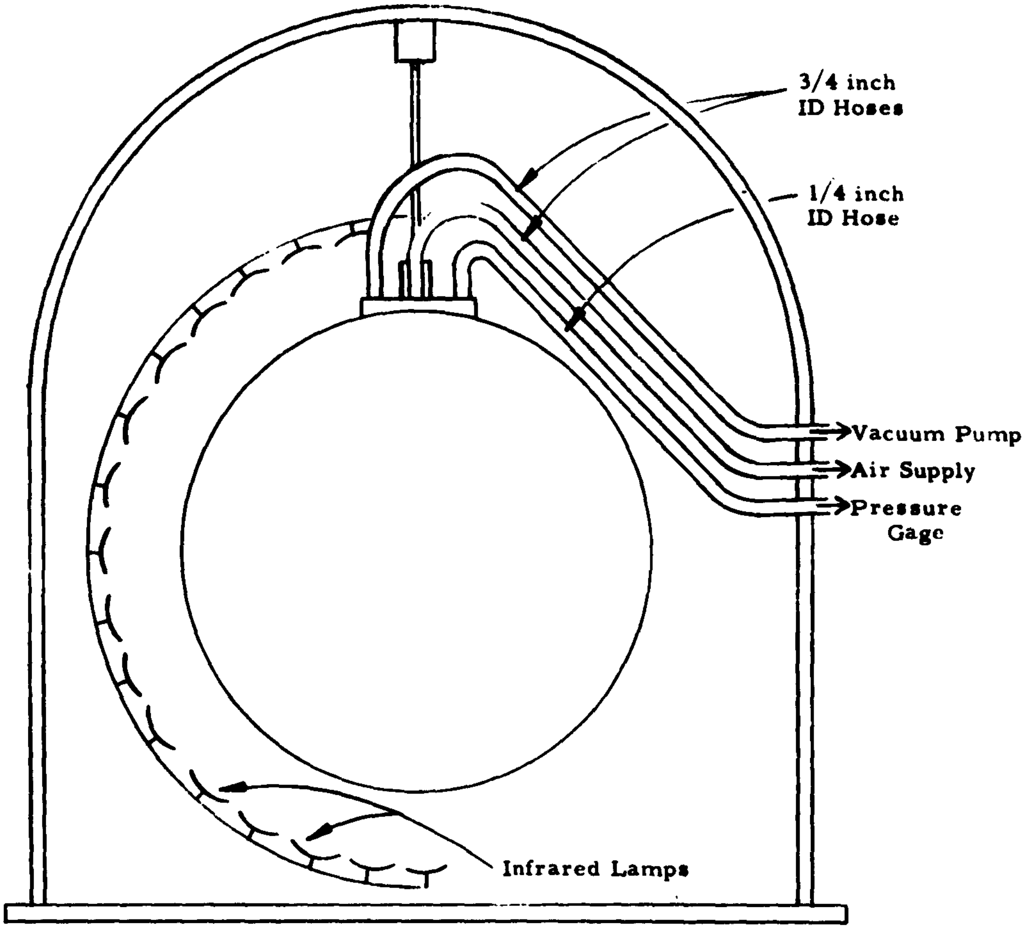


Figure 30. Set-up for inflating and controlling pressure in balloon during rigidization.

Figure 31. View of sphere, altitude facility and heating assembly.

Figure 32. Arrangement for heating segment of seven-foot diameter balloon for rigidization. USAF/ASD photo.

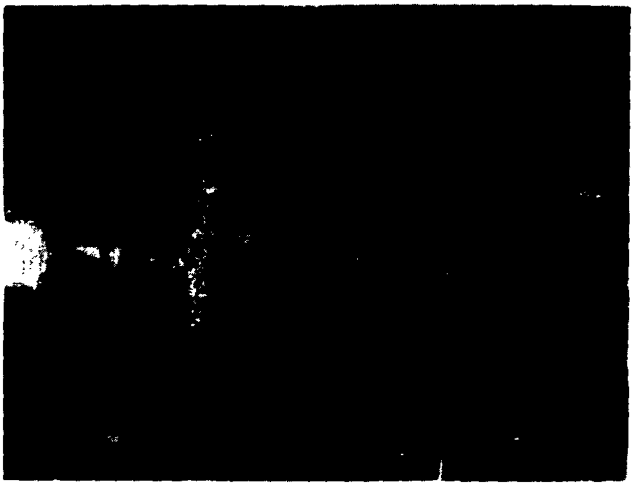


Figure 33a. The balloon is rotating to the left. The unfoamed material is out of range of the heat lamps and can be seen to the right. USAF/ASD photo.

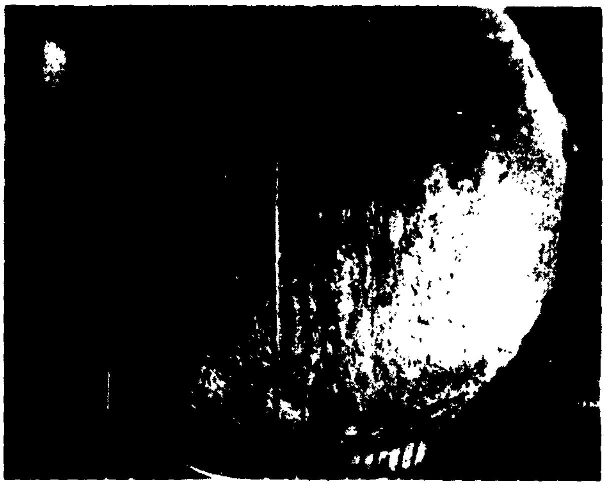


Figure 33b. Typical surface area of the rigidized structure. USAF/ASD photo.

Figure 34. The rigidized structure resting on pads. Very little distortion was found. USAF/ASD photo.

Figure 35. Close-up view of balloon wall thickness and section of heating assembly.

V. SUMMARY OF OBSERVATIONS

1. The concept of utilizing chemically blocked isocyanates was unsuccessful because: (a) excessively high temperatures (above 300°F) were required to cause cleavage and (b) at the cleavage temperature the vapor pressures of the blocking agent and the isocyanate were so high, relatively, that the material when tested in a vacuum (0.7 mm Hg) frothed excessively and literally "blew" itself apart.

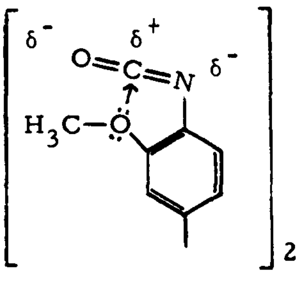
2. Since the primary object of the project was to produce a material which would foam at approximately 0.7 mm Hg (165,000 feet) almost all the tests of the foam powders were conducted at that pressure. Of the tests which were not conducted at 0.7 mm Hg, the majority were conducted at ambient atmospheric pressures, with but a very few tests made at intermediate pressures. It was therefore not possible to determine any but the most qualitative observations concerning the relationships between vapor pressures and the ambient pressures. However, it was noted that materials which foamed very slightly or not at all when heated at room pressures, and did foam at 0.7 mm Hg, also did not commence to foam until the pressure was lowered significantly from normal pressures; i.e., until pressures were lowered to approximately 100 to 50 mm very little evidence of foaming appeared. As the pressure was lowered the extent of foaming increased. Only one test was run at approximately 1×10^{-5} mm Hg using the 67-3 material which normally foamed well at 0.7 mm Hg. A fair foam was achieved, although it was somewhat lower in density than the same material foamed at 0.7 mm Hg. As a result of these limited tests it can be surmised that an environmental pressure change from 760 mm to approximately 50 mm represents a much greater change than does the change from 50 mm to 1×10^{-5} It can then further be surmised that a material which foams well at approximately 1 mm Hg should then foam well at much lower vacuums.

It must always be borne in mind however, that a number of other factors are involved in the formation of the foam. Properties such as the viscosity of the melt, the heating rate and the reaction rate must all be carefully balanced in order to produce the foam, i.e., a low viscosity material which reacts very rapidly, quickly becomes highly viscous before a foam can develop and either foams very little or forms one large bubble, regardless of the apparent vapor pressure. A material which is highly viscous when molten, could be made to foam in a vacuum if a blowing agent is added to the mixture, and if the reaction rate is slow enough to allow the foam to develop. On the other hand, slow reacting mixtures with obviously very high vapor pressures (at the heating temperature) frothed excessively in a vacuum, while foaming satisfactorily at the same temperature at a normal pressure. The presence of a relationship between the vapor pressure of the mixture and the surrounding pressures is therefore established, but unfortunately not enough time was available to determine the vapor pressures required to cause foaming in various pressure environments.

3. The use of encapsulating techniques to physically entrap isocyanate components was not satisfactory due in part to the inhibiting effect of the encapsulant. The results of tests of molecular sieves containing isocyanates were also not considered conclusive.

4. In the preparation of large quantities of the number 67-3 formula it was not found possible to homogeneously mix and grind the powders, unless the materials are "worked" and allowed to pre-react. There is a temperature rise during the pre-reaction step, and on cooling the material is hard and brittle, and can then be ground up. On subsequent heating and foaming the "pre-reacted" material, however, appears to react and foam as rapidly as material mixed without the pre-reaction step.

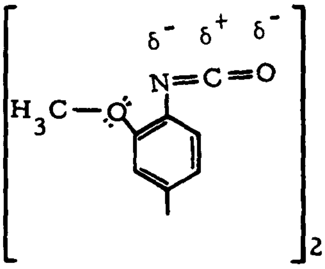
It should be emphasized that the "pre-reaction" step should not be considered as one which "uses" up all the exothermic reactivity of the isocyanate, since the DADI is a naturally slow reacting material, and thus the reaction can be easily stopped. As can be seen by observation of the structural formula of DADI the reactivity of the isocyanate grouping may be inhibited by steric hindrance, by electronic effects or both simultaneously. This is illustrated below:



---

*δ indicates small charge distributions. ↑indicates the association of the non-bonding electrons of the methoxy group with the positively charged carbon atom in isocyanate group.

Due to interaction of the ortho methoxy groups with the electropositive carbon atoms of the isocyanate groups, the latter are thus held in their most sterically hindered position;without this effect the compound could have the following configuration:



The above compound would then be much less susceptible to steric hindrance effects by the ortho substituent. In an examination of the analogous compound, 3, 3 dimethyl p-p' diphenyldiisocyanate (TODI) this neighboring group association does not occur and the compound is thus more reactive than the 3, 3' dimethoxy analogue (DADI).

In addition to this steric factor it should be noted that the association discussed above also tends to reduce the electropositive character of the carbon atom in the isocyanate group. Since these are the sites where basic catalysts attack, the reduced electropositive character of these sites makes them less sensitive to catalysts. Both of these effects then explain the low exothermic nature of the reaction.

From the above explanation of the steric hindrance-electronics effects which cause the low reactivity of the DADI, it should not be inferred that such low reactivity is necessarily a detriment. It is precisely the fact that the material has these reaction inhibiting characteristics which allows a slight pre-reaction to take place, which can be easily stopped by cooling. Furthermore it is also the steric hindrance (plus the relatively high melting point) which allows the material to be intimately mixed for long periods of time with other solid components and with catalyst with no reaction or even sensitivity to water vapor in the air

5. Because of the essentially endothermic nature of the powder a limit exists on the amount of powder which can be foamed. This limit was found to be approximately 1/2 inch of material, which resulted in foam of approximately 4-inch thickness. Attempts to make greater thicknesses of foam results in foaming at the top surfaces of the powder with unreacted material underneath which is shielded from heat by the foam material on top.

VI. CONCLUSIONS

1. The feasibility of producing a foamed urethane from all solid reactants has been established. The one part heat triggered reactant system is capable of foaming at reduced pressures and at atmospheric pressures by the addition of a water source.

2. Additional work will be required to develop a material which meets all the requirements of aerospace applications.

A. RECOMMENDATIONS

Since the material prepared under this project is not considered a perfected product, a number of recommendations may be made for future efforts which should result in a much improved product. These recommendations include:

1. Better methods of applying the material to a substrate are required. A preferred technique might be a calendered product, i.e., a flexible resin applied to a fabric skin. The seams, in a fabricated structure could be coated by hand spreading the material.

2. A method of triggering an exothermic reaction should be perfected. This could eliminate the current dependence on the heat source.

3. In the event that a stable, premixed exothermic material can not be prepared then a method of automatically heating and cooling the current material in space should be perfected. Such a system might well be a coating with high initial absorptivity, and low emissivity, which after 24 hours turns to low absorptivity and high emissivity. Application of this coating to the outer surface of the foam, prior to foaming, could result in a high temperature at first in space, and then later after foaming and rigidization, the material would cool down.

4. A complete determination of physical properties of the foam should be made so this information will be available for design purposes. This investigation should include all mechanical, thermal and electrical properties and, if possible, determination of the effectiveness of the material as a barrier to micrometeorite penetration and radiation encountered

in a space environment. This project should in addition include a determination of optimum forming conditions, i.e., temperature cycles and times required to obtain various physical properties.

5. Additional work should be done on determination of better catalyst systems. Currently the material liquifys and "boils" for several minutes prior to "setting." During this period vapors are emitted, which are lost, due to the low viscosity of the liquid resin. Catalyst systems, or possibly different resins, which would cause thickening in a shorter period of time would utilize these vapors to form light, probably finer pored foam.

6. Efforts should be made to determine the capabilities of the material and properties when foamed at higher vacuums.

APPENDIX

LABORATORY SYNTHESIS PROCEDURES

The laboratory procedures used to produce the prepolymers, blocked isocvnates, special hydroxides, and polyesters are given below.

Reaction of Diethylmalonate with 2, 4-Toluenediisocyanate (B3615-30B)

Sodium wire (4.6 gm., 0.2 mole) was slurried in dry ether (150 ml.) and diethylmalonate (32 gm., 0.2 mole) was slowly added. When hydrogen evolution ceased, toluene-2, 4-diisocyanate (17.4 gm., 0.1 mole) in ether (100 ml.) was slowly added. After stirring overnight, the precipitated product was collected by filtration, dissolved in ice water, precipitated by acidification with acetic acid, filtered, and the adduct rinsed with methanol. Vacuum drying yielded a product melting at 101°C.

Reaction of Acetylacetone with Diphenylmethane-p, p'-diisocyanate (B3615-30A and B)

Acetylacetone (0.2 mole, 20 gm.), ethyl ether (50 ml.), and diphenylmethane-p, p'-diisocyanate (0.1 mole, 25 gm.) were mixed together and sodium methylate (0.2 mole, 10.8 gm.) in methanol (200 ml.) was slowly added. The reaction occurred rapidly and after stirring several hours the solution was dissolved in water, and acidified with acetic acid. The precipitated adduct was collected by filtration and dried in vacuum. In an analogous experiment triethylamine was found to be an unsatisfactory catalyst.

Reaction of Toluenediisocyanate with Phthalimide (3615-32-4)

A solution of phthalimide (14.7 gm., 0.1 mole) and toluene-2, 4-diisocyanate (8.7 gm., 0.05 mole) in acetone (150 ml.) was stirred for 18 hours at 25°C. The precipitated product was collected by filtration, thoroughly washed with acetone, and dried in vacuum.

In an analogous experiment the 1:1 adduct was prepared using phthalimide (14.7 gm., 0.1 mole) and toluene diisocyanate (26 gm., 0.15 mole).

Reaction of Toluenediisocyanate with Sodium Bisulfite (3615-32)

To a solution of sodium bisulfite (52 gm., 0.5 mole) in water (100 ml.) was added toluene-2, 4-diisocyanate (44 gm., 0.25 mole). The mixture was stirred while maintaining the temperature below 65°C. Above 65°C the isocyanate compound reacts with water; however, below this temperature the reaction proceeds to yield the bisulfite adduct. After four to six hours the white solid product is collected by filtration and vacuum dried.

Reaction of p-Nitrophenol with Diphenylmethane-p, p'-diisocyanate (3615-37)

p-Nitrophenol (14 gm., 0.1 mole) and p, p'-diphenylmethanediisocyanate (12.5 gm., 0.05 mole) were dissolved in benzene (100 ml.) and heated at reflux for 1/2 hour. The yellow product which was collected by filtration and dried in vacuum, melted at 175-80°C. The adduct exhibited no tendency to dissociate below 160°C when formulated with catalyzed commercial polyols and its rate of dissociation was unsatisfactory for vacuum foaming applications.

Reaction of Picric Acid with Toluenediisocyanate (3615-38)

A solution of picric acid (2.3 gms., 0.01 mole), toluene-2, 4-diisocyanate (1.8 gm., 0.01 mole) and benzene (15 ml.) was heated at reflux for 20 hours. After removal of the benzene by vacuum distillation an ethanol insoluble product was obtained which melted above 200°C. The product was not evaluated further since it did not appear to unblock.

Isocyanate "Blocking" with t-Amyl Alcohol

A typical investigation on tertiary alcohols involved the reaction of a polyol (Archer-Daniels-Midland, Arapol 7825, 30.5 gm., 0.2 eq. OH), a polyisocyanate (ADM, Arapol 7845, 9.2 gm., 0.1 eq. NCO) and t-amylalcohol (0.1 eq. OH, 8.8 gm.). The reaction was performed at about 5°C. After 24 hours samples of the very viscous mixture were heated at various temperatures to determine the preferred cleavage temperature (130°C to 140°C). The slightly soft foamed structure hardened completely on cooling. When samples of this material were heated in vacuum the foaming process was uncontrolable. Other formulations having different ratios of these ingredients were also prepared but similar results were obtained.

Synthesis of Benzyldimethylcarbinol (2352-23)

To a slurry of magnesium (55 gm., 2.3 mole) in dry ether (3.39 gm) was slowly added benzyl chloride over a 4-hour period. The reaction required several iodine crystals for initiation. After only 75 percent of the benzyl chloride had been used additional ether (700 ml.) was added followed by dry acetone (116 gm.) and the reaction stirred overnight. The mixture was hydrolyzed with ammonium chloride solution (110 gm. per 700 ml.H_2O), then acidified with 10 percent H_2SO_4 to a pH of 6-7. The ether phase was collected, dried with K_2CO_3, and distilled to yield benzyldimethylcarbinol (110 gm., 50 percent yield, B.P.$_4$ 67-68°C, n_D^{25} = 1.5115) and 1, 2 diphenylethane (54 gm., m.p. 51°C, 30 percent yield, recrystallized from methanol).

Isocyanate "Blocking" with Benzyldimethylcarbinol

Benzyldimethylcarbinol (0.1 mole) was reacted at 5°C with a polyisocyanate (Archer Daniels Arapol 7825, 0.2 eq.) catalyzed by triethyl amine (4 drops). The reaction product was then formulated with additional polyisocyanate (Arapol 7825, 0.1 eq.) and a poly ether polyol (Arapol 7845, 0.1 eq.). A study of the decomposition temperature of the formulations showed that no significant CO_2 evolution occurred until a temperature of 130-170°C was reached.

Preparation of Lead Hydroxide

To a solution of lead nitrate (30 gm.) in water, concentrated ammonium hydroxide was gradually added until the pH was 9. The precipitate was thoroughly water washed, and dried in vacuum for 17 hours at 30°C. No further weight loss occurred in 3 additional hours. Sample ignition showed this hydroxide to have 2.84 percent H_2O (theoretical 7.46 percent).

Preparation of Zinc Hydroxide

Concentrated ammonium hydroxide was gradually added to a solution of zinc chloride (43.5 gm.) in water (100 gm.) until the pH was 6. The precipitate was collected by filtration, washed and vacuum dried for 20 hours at 65°C. Sample ignition for 18 hours at 300°C showed this hydroxide to contain 14.52 percent water (theoretical 18.11 percent).

Preparation of Bismuth Hydroxide

Bismuth nitrate (48.5 gm.) was dissolved in a 25 percent solution of nitric acid (100 ml.). The solution was poured into a mixture of concentrated ammonium hydroxide (50 ml.) and hydrogen peroxide (4 percent, 100 ml.) resulting in the formation of a precipitate which was collected by filtration washed with additional peroxide-hydroxide mixture, followed by washing with hot dilute ammonium hydroxide (1.8 percent). The above procedure failed to yield the desired product but instead yielded bismuth subnitrate.

Reaction of Neopentylglycol with Diphenylmethane-p, p'diisocyanate

To a solution of diphenylmethane-p, p'diisocyanate, (50 gm., 0.2 mole) in ether (250 ml.) was slowly added a solution of neopentylglycol (10.4 gm., 0.1 mole) in ether (100 ml.). The reaction was catalyzed by triethylamine (1/2 ml.). After stirring overnight, a solid precipitate had formed which was collected by filtration and vacuum dried. It melted above 200°C.

Reaction of Ethanolamine with Diphenic Acid (B4015-5)

A solution of o, o'biphenyldicarboxylic acid (diphenic acid, 18 gm., 0.075 mole) was dissolved in methyl alcohol (150 ml.) containing a catalyst (0.2 ml. H_2SO_4). After stirring at reflux for 20 hours the catalyst was neutralized with triethylamine (1 gm.). Ethanolamine (12 gm., 0.2 mole) was then added and the solution was heated at reflux for 2 hours.

The methanol was removed by distillation and the remaining product was washed with water to remove the excess ethanolamine and methanol. This procedure proved unsatisfactory since the desired product washed out and was lost.

Reaction of Neopentylglycol with m, m'-Dimethyl-p, p'-biphenyldiisocyanate (2297-43)

To a solution of m, m'-dimethyl-p, p'-biphenyldiisocyanate (0.2 mole, 53 gm.) in ether (500 ml.) was slowly added a solution of neopentyl glycol (0.08 mole, 8 gm.) in ether (200 ml.). The solution was heated for 20 hours, resulting in the precipitation of a white solid product which, when collected by filtration and dried in vacuum, melted at 170°C.

Reaction of o-Hydroxybenzyl Alcohol with Diphenic Acid (2297-47)

A solution of diphenic acid (o, o'-biphenyldicarboxylic acid, 18 gm., 0.075 mole) o-hydroxybenzyl alcohol (0.15 mole, 18.6 gm.) sulfuric acid (5 drops) and toluene (200 ml.) was heated at reflux under azeotropic distillation for 3 hours, after which time the theoretical amount of water had been liberated. An infusible solid product precipitated after a short time, and was collected by filtration. It was later found that the product was a phenol formaldehyde polymer.

Reaction of Neopentylglycol with Toluenediisocyanate (2297-48)

To a solution of toluene-2, 4-diisocyanate (17.4 gm., 0.1mole) in ether (200 ml.) was gradually added a solution of neopentyl glycol (0.2 mole, 20.8 gm.) in ether (100 ml.). The mixture was heated at reflux for 20 hours. Removal of the ether by distillation yielded a viscuous liquid product.

Preparation of the Ethanolamide of Diphenic Acid (2297-49)

A solution of diphenic acid (0.1 mole, 24.2 gm.) and ethanolamine (0.2 mole, 12.2 gm.) in methanol (100 ml.) was prepared and the mixture heated at reflux for several hours. Methanol was then removed by distillation and the reaction product gradually heated to 160°C, at which temperature it was maintained for 40 hours. The liquid product remained water soluble and the reaction failed to go to completion.

Preparation of N, N'-Bishydroxyethylsebacamide (2297-51)

A solution of Sebacoyl chloride (0.1 mole), ethanolamine (0.40 mole, 24 gm.) and dioxane (500 ml.) was heated at reflux for 2 hours. Upon cooling, the reaction mixture solidified to a mass of crystals which were recovered by filtration, carefully washed with small amounts of water to remove the ethanolamine hydrochloride, and recrystallized from dioxane to give a product melting at 148-150°C.

Reaction of Ethyleneglycol with Diphenylmethane-p, p'diisocyanate (B2351-19B)

To a solution of diphenylmethane-p, p'-diisocyanate (0.1 mole, 25 gm.) in dioxane was added ethylene glycol (0.05 mole, 3.1 gm.). The solution was stirred magnetically until it stopped due to the precipitation of the product. The following day the dioxane was removed by vacuum distillation and the solid product collected. Its m.p. was above 250°C.

Reaction of Trismethylolaminomethane with Toluenediisocyanate (B2351-18C)

A slurry of trismethylolaminomethane (0.2 mole, 24 gm.) and 2, 4-toluenediisocyanate (0.1 mole, 17.4 gm.) in ether (500 ml.) was stirred together for one week. At the end of this time the ether was distilled off. The remaining solid product was infusible due to crosslinking. It is worthy of note that if a satisfactory mutual solvent had been found, the reaction could have proceeded smoothly.

Reaction of Tris(hydroxymethyl)propane with toluenediisocyanate (B2351-18B)

To a solution of toluene-2, 4-diisocyanate (0.22 mole, 38 gm.) in ether (150 ml.) was added a solution of 1, 1, 1-tris(hydroxymethyl) propane (0.1 mole, 13.49 gm.) in ether (100 ml.). The reaction was catalyzed with several drops of triethyl amine. After maintaining the reaction mixture at reflux for 4 hours the mixture was cooled and stirred overnight. Filtration of the product followed by vacuum drying yielded a nonfusible solid (50 gm.), due to excessive crosslinking through the available NCO groups.

Reaction of Neopentylglycol with Diphenic Acid (B3615-14)

A solution of neopentyl glycol (0.2 mole, 20.4 gm.), diphenic acid (18 gm., 0.075 mole), sulfuric acid (0.5 ml.) and toluene (200 ml.) was heated at reflux until the theoretical amount of water was liberated and trapped in an azeotropic trap. After completion of the reaction the solution was washed with saturated sodium carbonate solution and dried with magnesium sulfate. The solvent was then removed by vacuum distillation. Although a great deal of difficulty was encountered trying to recrystallize the produce, a small sample of crystals was obtained from a mixture of petroleum ether and chloroform. The solid melted at 53°C.

Preparation of Neopentylglycoladipate (3615-15)

A solution of neopentyl glycol (0.2 mole, 20.8 gm), adipic acid (0.075 mole, 11.0 gm.), sulfuric acid (0.5 ml.), and toluene (150 ml.) was heated at reflux until the theoretical amount of water (2.7 ml.) was collected in an azeotropic trap. Upon completion of the reaction the mixture was thoroughly washed with saturated sodium carbonate solution and the solvent was completely removed by vacuum distillation. The diol ester thus prepared was a liquid.

Preparation of Triphenylmethane-p, p', p''-tris-2-hydroxethylurethane (B3615-39)

A solution of triphenylmethane-p, p', p''-triisocyanate (0.03 mole, 11 gm.) in dioxane (25 ml.) was added to a solution of ethylene glycol (11 gm., 0.18 mole), in dioxane (75 ml.) and several drops of triethylamine were added. The reaction was maintained at 80-90°C for 20 hours. After completion of the reaction the dioxane was removed by distillation and the product poured into water (50 ml.) to extract the excess ethylene glycol. An oily product separated from the aqueous solution and was collected. Efforts were made to crystallize the oil but without success.

Preparation of N, N'Bis(hydroxyethyl)sebacamide (B2351-19A)

To a solution of ethanolamine (6 gm., 0.10 mole) and triethylamine (10 gm., 0.1 mole) in dioxane (80 ml.), was slowly added sebacoyl chloride (12 gm., 0.05 mole). The thick hot paste was diluted with additional dioxane (100 ml.) and heated to reflux. The hazy solution was clarified by the addition of additional ethanolamine (3 gm., 0.05 mole). After several hours at reflux the mixture was poured into a large volume of water (600 ml.) thus precipitating the product. Recrystallization of the solid from a mixture of chloroform and methanol yielded a compound melting at 150°C. The yield was poor, apparently due to loss of much product failing to crystallize from the water dioxane solution.

Reaction of 2, 2-Bis(4-hydroxycyclohexyl)propane with Fumaric Acid

A mixture of 2, 2-bis(4-hydroxycyclohexyl) propane (0.2 mole, 48 gm.), fumaric acid (0.1 mole, 11.6 gm.), p-toluene sulfonic acid (0.4 gm.) and xylene (200 ml.) was heated at reflux until a quantitative amount of water was collected in an azeotropic trap. Upon completion of the reaction, a solution of KOH (0.12 gm.) in methanol (2 ml.) was added to neutralize the catalyst. Removal of the solvent by vacuum distillation yielded a brittle glassy product having a softening point of 50-55°C. The product failed to react with isocyanate compounds, indicating that cyclization had occurred.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Terphthaloyl Chloride (3615-41B)

To a solution of 2, 2-bis(4-hydroxycyclohexyl)propane (0.4 mole, 96 gm.) in benzene (200 ml.) was slowly added a solution of terphthaloyl chloride (0.2 mole) in benzene (100 ml.). After refluxing overnight the gelatinous precipitate was dried in vacuum and ground in a mortar to yield a solid melting at 150°C.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Azelaic Acid (B2351-21)

A mixture of 2, 2-bis(4-hydroxycyclohexyl)propane (48 gm., 0.2 mole), azelaic acid (18.8 gm., 0.1 mole), and toluene sulfonic acid (0.19gm.)

in benzene (250 ml.) was heated at reflux for 20 hours. Since only 1.6 ml. of H_2O had separated by azeotropic distillation, additional catalyst (0.2 gm.) was added and heating continued for 44 hours until the reaction was complete (3.6 ml. H_2O formed). After removal of the major portion of solvent by normal distillation the remaining solvent was removed by prolonged heating (150°C) under reduced pressure (0.1 mm), thus yielding a viscous liquid product.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Adipic Acid

A mixture of 2, 2-bis(4-hydroxycyclohexyl)propane (0.4 mole, 96 gm.), adipic acid (0.2 mole, 29.2 gm.), sulfuric acid (15 drops) and toluene (300 ml.) was heated at reflux until water liberation ceased.(5.4 ml.). After the catalyst was neutralized with a solution of KOH (0.36 gm.) in methanol (3 ml.) the solvent was removed by vacuum distillation yielding a glassy brittle product having a softening point near 60°C.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Malonic Acid (B4015-9)

A solution of 2, 2-bis(4-hydroxycyclohexyl)propane (48 gm., 0.2 mole), malonic acid (14.5 gm., 0.14 mole), p-toluene sulfonic acid (1 gm.) and toluene (500 ml.) was heated at reflux until the theoretical amount of water had been trapped in an azeotropic trap (5-1/2 hours). A solution of potassium hydroxide (0.25 gm.) in methanol (3 ml.) was then added to neutralize the acid catalyst. Removal of the solvent with heat (to 140°C) and vacuum (0.1 mm Hg) yielded a glassy product softening at 55-60°C. The very low reactivity of this product toward isocyanate compounds indicated that the desired product was not obtained, but rather that a cyclized product had formed.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Succinic Acid (B4015-9)

A solution of 2, 2-bis(4-hydroxycyclohexyl)propane (0.4 mole, 96 gm.), succinic acid (29 gm., 0.24 mole), toluene sulfonic acid (0.003gm.) and benzene (200 ml.) was heated under azeotropic distillation until the theoretical amount of water had been liberated (8.5 ml.). Upon completion of the reaction, a solution of potassium hydroxide (0.17 gm.) in methanol (3 ml.) was added. Solvent removal was accomplished by heating (150°) under vacuum (0.1 mm Hg). A brittle glassy product was obtained. The powdered product had a softening point of 55-60°C.

Reaction of Hexamethyleneglycol with Diphenylmethane-p, p'diisocyanate (3615-34, 46, and 51)

Solutions of diphenylmethane-p, p'-diisocyanate (0.2 mole, 0.3 mole, and 0.4 mole) and 1,6 hexanediol (0.1 mole) in benzene (100 ml.) were heated at reflux for 4 hours. Each of the three reactions yielded a white solid product which was collected by filtration and dried in vacuum. The 2:1 product had a melting point over 200°C, the 3:1 product melted at 120-130°C and the 4:1 product melted at 105-110°C. It should be noted that the 3:1 and 4:1 products actually are only mixtures of 2:1 product with excess unreacted diphenylmethane-p, p'-diisocyanate.

Preparation of Solid Polyisocyanates by Devolatilization

Archer Daniels Arapol 7825 and Reichold 8625 prepolymers were slowly passed through a molecular still (at 150°C and 0.2 mm Hg) to remove all traces of unreacted monomers. The devolatilized Arapol 7825 was a viscous liquid, whereas the devolatilized Reichold 8625 was an amber colored brittle glass having a melting point of 83-86°C and an equivalent weight of 218. This solid was readily ground into a powder.

Synthesis of the Sebacamide of Aminomethylpropanediol (B4015-11)

To a solution of 2-amino-2-methyl-1, 3-propanediol (0.15 mole, 15.8 gms.) and triethylamine (0.05 mole, 5.0 gm.) in dioxane (200 ml.) was slowly added a solution of sebacyl chloride (0.05 mole, 12.0 gm.) in dioxane (50 ml.). The mixture was refluxed for 1-1/2 hours and the dioxane (195 ml.) was then removed by distillation. Sufficient NaOH (in methanol) was then added to neutralize the triethylamine hydrochloride which was then ex racted with benzene. Upon removal of the residual solvents on a molecular still a solid product was isolated;

however, no satisfactory solvent could be found for recrystallizing this extremely water soluble product. An approximate melting point of 104°C was noted on the impure material.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Succinic Acid (B2351-20)

2-2-bis(4-hydroxycyclohexyl)propane (59.5 gm., 0.248 mole), succinic acid (14.6 gm., 0.124 mole), and sulfuric acid (10 drops) were dissolved in toluene (250 ml.) and heated at reflux with an azeotropic trap until 5 ml. of water had been liberated. The solvent (170 ml.) was then distilled off and the H_2SO_4 neutralized with powdered KOH (0.3 gm.). The mix was diluted with methanol (1 L) to precipitate the unreacted 2, 2-bis(4-hydroxycyclohexyl)propane and the methanol was then removed by vacuum distillation at 48-52°C. The product was then completely freed of solvents by heating at 150°C (1 mm Hg) for several hours. A brittle glassy product (m.p. 50-60°C) was then obtained.

Esterification of 2, 2-Bis(4-hydroxycyclohexyl)propane with Sebacyl Chloride (B2351-18)

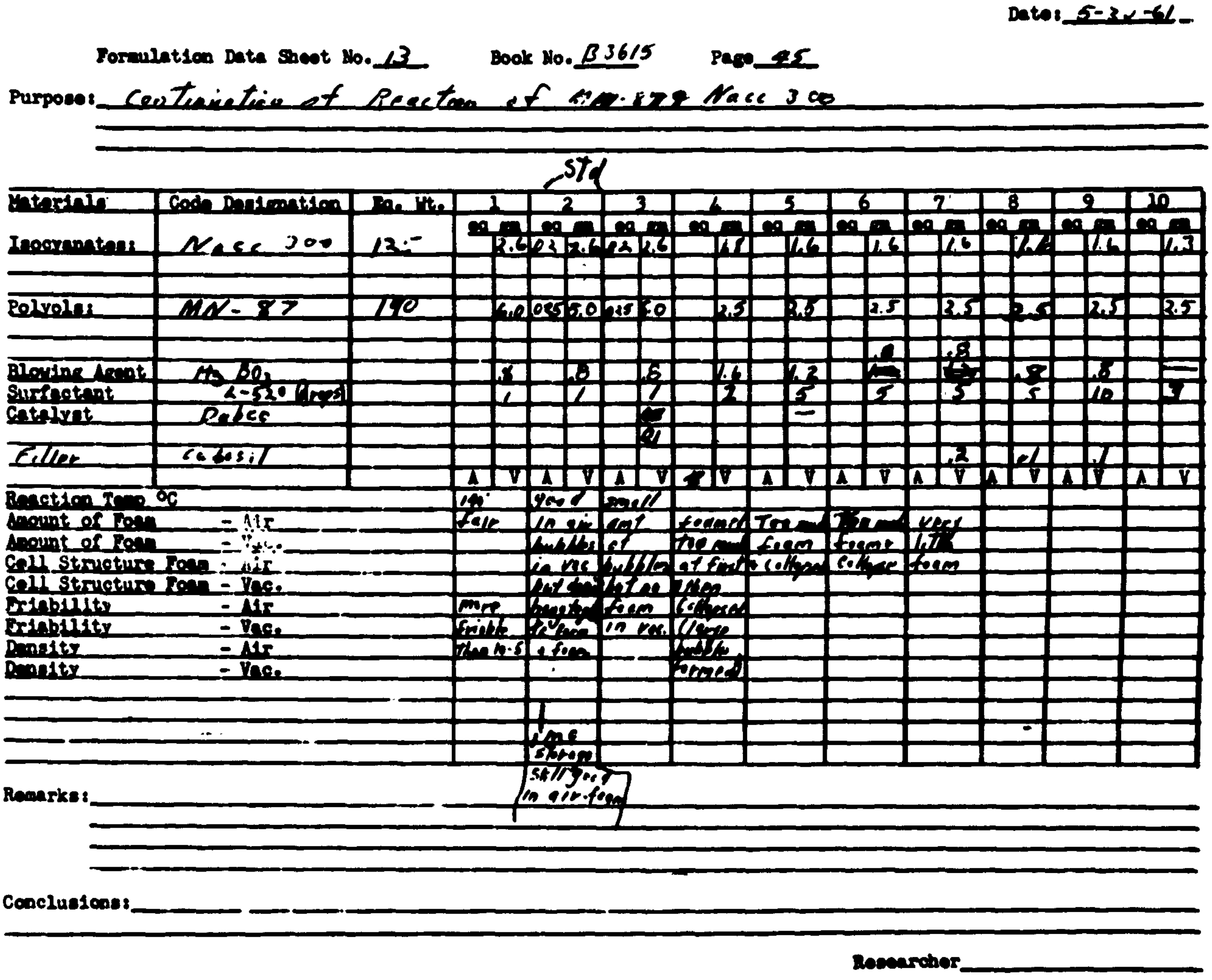
A solution of 2, 2-bis(4-hydroxycyclohexyl)propane (0.12 mole, 27.4 gm.), sebacyl chloride (0.05 mole, 12 gm.), and benzene (250 ml.) was heated at reflux for 15 hours. Pyridine (11 ml.) was added and heating was continued (46 hours). The reaction mixture was thoroughly washed with saturated $NaHCO_3$ solution then with water. Removal of the solvent on a molecular still yielded a viscous liquid product.

Reaction of Mobay Multron R-14 and diphenylmethane-p, p'diisocyanate (B3515-45B)

Mobay R-14, a polyester with an equivalent weight of 1000, 0. mole, 100 gm and diphenylmethane, -p, p'diisocyanate 0. 134 mole, 16. 7 gm, ground up together to form a fine powder. Add 3-1/2 gms Dabco catalyst. Material when heated melts to form a tough, rubbery product. Note that isocyanate is added in excess of stoichiometrical quantity. No data on shelf life of mixture.

FORMULATION PROCEDURES

Listing the many formulations individually in a lab notebook was considered an unwieldy method of notekeeping. Consequently a formulation data sheet was devised which could be used to note ten variations of any basic formula, which was kept in a bound notebook. An example of such a sheet is shown below.



Date: 5-2?-61

Formulation Data Sheet No. 13 **Book No.** B3615 **Page** 45

Purpose: Continuation of Reaction of MN-87 & Nacc 300

Std (over run 2)

Materials	Code Designation	Eq. Wt.	1		2		3		4		5		6		7		8		9		10	
			eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm	eq	gm
Isocyanates:	Nacc 300	135		2.6	.023	2.6	.022	2.6		1.8		1.6		1.6		1.6		1.6		1.6		1.3
Polyols:	MN-87	190		6.0	.025	5.0	.025	5.0		2.5		2.5		2.5		2.5		2.5		2.5		2.5
														.8		.8						
Blowing Agent	H₂BO₃			.8		.8		.6		1.6		1.2		[illegible]		[illegible]		.8		.8		—
Surfactant	L-520 (drops)			1		1		7		2		5		5		5		5		10		7
Catalyst	Dabco							[illegible]				—										
								.01														
Filler	Cabosil															.2		.1		.1		
			A	V	A	V	A	V	A	V	A	V	A	V	A	V	A	V	A	V	A	V
Reaction Temp °C			140°		good		small															
Amount of Foam - Air			fair		in air		amt		foamed		Too much		Too much		very							
Amount of Foam - Vac.					bubbles		of		too much		foam		foam		little							
Cell Structure Foam - Air					in vac		bubbles		at first		collapsed		collapse		foam							
Cell Structure Foam - Vac.					but don't		but no		then													
Friability - Air			more		[illegible]		foam		collapsed													
Friability - Vac.			friable		[illegible]		in vac.		(large													
Density - Air			than N-5		a foam				bubbles													
Density - Vac.									formed)													
					fine																	
					strong																	

Skin good in air foam

Remarks:

Conclusions:

Researcher

BIBLIOGRAPHY

1. Arnold, R. G., Nelson, J. A., and Verbanc, J. J., "Chemistry of Organic Isocyanates," E. I. duPont de Nemours Co., Elastomer Chemicals Department Publication HR-2, 20 January 1956.

2. Petersen, S., "Reaction Products of Aliphatic Diisocyanates," Annalen, vol. 562, p. 205, 1949.

3. Saunders, J. H. and Slocombe, R. J., "The Chemistry of the Organic Isocyanates," Chemical Reviews, vol. 43, p. 203, 1948.

4. Saunders, J. H., "The Reactions of Isocyanates and Isocyanate Derivatives at Elevated Temperatures," Rubber Chemistry and Technology, vol. 32, p. 2, April - June 1959.

5. Saunders, J. H., "The Formation of Urethane Forms," Rubber Chemistry and Technology, vol. 33, p. 5, December 1960.

6. "Urethane Polymers," Encyclopedia of Chemical Technology, First Supplement Volume, 1957.

7. Heiss, H. L., Saunders, J. H., Morris, M. R., Davis, B. R. and Hardy, E. E., "Preparation of Polymers from Diisocyanates and Polyols," Industrial and Engineering Chemistry, vol. 46, p. 1498, July 1954.

8. Heiss, H. L., Combs, F. P., Gemeinhardt, P. G., Saunders, J. H., and Hardy, E. E., "Influence of Acids and Bases on Preparation of Urethane Polymers," Industrial and Engineering Chemistry, vol. 51, p. 929, August 1954.

9. McElroy, W. R., "The Techniques of Prepolymer Preparation," Mobay Chemical Co.

10. "Urethane Surface Coatings," Mobay Chemical Co.

11. "Urethane Foam", Technical Information Bulletins, Mobay Chemical Co.

12. D'Ancicco, V. V. "A New Family of Heat Resistant Urethane Polymers," Soc. of Plastics Engineers Journal, vol. 14, p. 2, February 1958.

13. Axelrood, S. L., and Frisch, K. C., "Cast Urethane Elastomers from Propylene Glycols," presented at April 1960 meeting of American Chemicals Society.

14. Barringer, C. M., "Rigid Urethane Foams, - II - Chemistry and Formulation," E. I. duPont de Nemours Elastomer Chemicals Department Bulletin HR-26, April 1958.

15. Smith, C. H. and Peterson, C. A., "Cast Flexible Urethane Polymers," Modern Plastics, p. 125, July 1961.

16. Wilson, J. E., "Sorbitol Polyethers in Rigid Urethane Foam," Modern Plastics, p. 151, May 1959.

17. Aylesworth, R. D., Boehringer, R. H., Moore, D. T., and Smith, M. H., "Polyesters of Dimer Acids as Intermediates for Urethane Foams," Modern Plastics, p. 145, May 1958.

18. Erner, W. E., Farkas, A., and Hill, P. W., "One-Shot Urethane Foam," Modern Plastics, p. 107, February 1960.

19. Dombrow, B. A., "Polyurethanes," Reinhold Publishing Corp., 1957.

20. Bolin, R. E., Szabat, J. F., Cote, R. J., Peters, E., Gemeinhardt, P. G., Morecraft, A. S., Hardy, E. E. and Saunders, J. H., "The Properties of Urethane Foams Related to the Calculated Molecular Weight Per Branch Point," American Chem. Soc. Meeting, Chicago, Ill., September 1958.

Aeronautical Systems Division, Dir/Materials and Processes, Applications Lab, Wright-Patterson AFB, Ohio.
Rpt Nr ASD-TDR-62-416. DELAYED ACTION, FOAM-IN-PLACE POLYURETHANE FOR USE IN AN AEROSPACE ENVIRONMENT.
Final report, Mar 63, 100p. incl illus., tables.
Unclassified Report

This report details the materials and techniques developed to meet the requirement of a delayed action, foam-in-place polyurethane for use in an aerospace environment. The methods investigated for preparation of the special polyurethane included a number of chemical blocking reactions, molecular sieves and encapsulation techniques, all designed as restraining agents to inhibit the activity of the isocyanate component. The successful method finally developed utilized the principle of solid components to assure low reactivity and good storability. The

(over)

optimum compound employed a sterically hindered solid diisocyanate, dianisidine diisocyanate, a solid diol, an ethylene oxide adduct of bisphenol A, a solid triol crosslinker, trimethylol propane, and a solid catalyst, dibutyl tin di-2-ethyl hexoate. The resulting powder mixture was found to have storage stability of at least two months when stored at room temperature. The powder could be activated to produce foams of 2 to 5 pounds per cubic foot density on heating to 175 to 250°F in a vacuum environment. By addition of a water liberating blowing agent, boric acid, foams can also be made under ambient pressure conditions. Structural components, made to demonstrate the utility of the powder, consisted of a seven-foot diameter balloon, which using predistributed powder on its surface, was inflated and rigidized at a simulated altitude of 150,000 feet, and a full sized man-supporting chair which was also made under the same conditions. In both cases infra-red heat was used as the triggering mechanism.

1. Astronautics
2. Interplanetary space flight
3. Structural elements
I. AFSC Project 7381, Task 738101
II. Contract AF 33(616)-7925
III. Hughes Aircraft Co., Culver City, Calif.
IV. S. Schwartz
V. Not aval fr OTS
VI. In ASTIA collection

Aeronautical Systems Division, Dir/Materials and Processes, Applications Lab, Wright-Patterson AFB, Ohio.
Rpt Nr ASD-TDR-62-416. DELAYED ACTION, FOAM-IN-PLACE POLYURETHANE FOR USE IN AN AEROSPACE ENVIRONMENT.
Final report, Mar 63, 100p. incl illus., tables.
Unclassified Report

This report details the materials and techniques developed to meet the requirement of a delayed action, foam-in-place polyurethane for use in an aerospace environment. The methods investigated for preparation of the special polyurethane included a number of chemical blocking reactions, molecular sieves and encapsulation techniques, all designed as restraining agents to inhibit the activity of the isocyanate component. The successful method finally developed utilized the principle of solid components to assure low reactivity and good storability. The

(over)

optimum compound employed a sterically hindered solid diisocyanate, dianisidine diisocyanate, a solid diol, an ethylene oxide adduct of bisphenol A, a solid triol crosslinker, trimethylol propane, and a solid catalyst, dibutyl tin di-2-ethyl hexoate. The resulting powder mixture was found to have storage stability of at least two months when stored at room temperature. The powder could be activated to produce foams of 2 to 5 pounds per cubic foot density on heating to 175 to 250°F in a vacuum environment. By addition of a water liberating blowing agent, boric acid, foams can also be made under ambient pressure conditions. Structural components, made to demonstrate the utility of the powder, consisted of a seven-foot diameter balloon, which using predistributed powder on its surface, was inflated and rigidized at a simulated altitude of 150,000 feet, and a full sized man-supporting chair which was also made under the same conditions. In both cases infra-red heat was used as the triggering mechanism.

1. Astronautics
2. Interplanetary space flight
3. Structural elements
I. AFSC Project 7381, Task 738101
II. Contract AF 33(616)-7925
III. Hughes Aircraft Co., Culver City, Calif.
IV. S. Schwartz
V. Not aval fr OTS
VI. In ASTIA collection